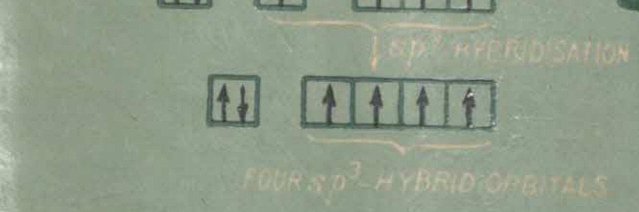
# General & Inorganic Chemistry



**S. N. PODDAR**
**&**
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$$_7N^{14} + {_2He^4} \longrightarrow [{_9F^{18}}] \longrightarrow {_8O^{17}} + {_1H^1}$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

$Fe(CN) + 4\,KCN = K\ [Fe\,(CN)\ ]\ [$ $]^{4-}$

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# GENERAL
# &
# INORGANIC CHEMISTRY

A TEXT BOOK FOR B.Sc. STUDENTS

**VOLUME I**

**REVISED AND ENLARGED SECOND EDITION**

**1988**

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To
Shanti

Vol. II of this book contains the Chemistry of elements of Groups IV, V, VI, VII and VIII.

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# PREFACE TO THE SECOND EDITION

Although the arrangement of the different topics and the basic approach of the text remains unchanged, we have revised and enlarged all the chapters on *general chemistry* in the light of the recent changes in the B.Sc (Pass) Syllabi of the Universities of Eastern India. In addition, each chapter on General Chemistry in supplimented by some new and somewhat advanced-level materials. All such advanced-level materials are presented in smaller prints and are placed in the text in such a manner that a less inquisitive student can skip them (if he desires to do so) without feeling the effect of discontinuity in the subject-matter. In order to compensate for the considerable increase in the volume of this edition due to extensive revision and remodelling, we have withdrawn the introductory portion of the first edition, "Introduction to Inorganic Chemistry".

Many of our friends and colleagues from different colleges and Universities have sent their comments and criticisms on our book and have helped us enormously in removing errors and inadequacies that normally creep into the first edition of a book. We offer our sincere thanks to all of them and we believe that they will continue to extend their helping hands in future.

We sincerely appreciate the painstaking and efficient efforts of M/s Book Syndicate Private Limited in the publication of this book in its present form.

Calcutta AUTHORS

31st January, 1988

# PREFACE TO THE FIRST EDITION

This book covers the B.Sc. (pass) course syllabi of most of the Indian Universities. It particularly covers the entire syllabi of general and inorganic chemistry of all the Universities of Eastern India. In the recent years, the under-graduate inorganic chemistry syllabi of all the Indian Universities have undergone a radical change, and in the syllabi of the Eastern Universities at present, there exists very little difference between the B.Sc. pass level and the corresponding honours course. This has made the writing of a text book on **general and inorganic chemistry** for the B.Sc. pass course a challenging task which necessarily required a simple and very lucid exposition of the comparatively difficult and complicated topics of general chemistry and descriptive inorganic chemistry, so long reserved for the more meritorious and much more serious students taking up the honours course.

In Eastern India, the new syllabi have been introduced since the past one year, but uptil now, not a single book is published which covers the entire new syllabi and is written in a way so as to implement the real objective behind the recent and rather drastic revision of the syllabi. When we undertook the task of writing this book, we were very much aware of the difficulties involved, but decided to make a serious attempt. Even though the standard of the subject has been raised rather sharply and even abruptly, it is a pleasure to find that the Universities have realised at last that, to learn inorganic chemistry, it is not sufficient to acquire a knowledge of the methods of preparation and properties of the elements and their compounds, the winning of the metals from their ores and similar empirical facts and figures. The students must have a firm grasp of the fundamental principles of general chemistry, such as the atomic structure, including the concepts of the different electronic energy levels, the size, shape and orientation of the orbitals and the electronic configuration of the elements. The principle of periodic classification of elements and its importance in elucidating the descriptive chemistry of the elements must be clearly understood. The actual causes behind the formation of different types of chemical bonds and the characteristics associated with each of them, the phenomenon of oxidation and reduction, acids and bases, the phenomenon of radioactivity and the formation, characteristics and structural aspects of coordination chemistry are of profound fundamental importance and must be thoroughly appreciated. The proper correlation between the chemical changes occurring and the physical and structural factors causing them (which can be clearly understood from the knowledge of the fundamental principles mentioned before) is infinitely more important than sheer memorisation of a huge jumble of apparently unrelated facts which becomes a heavy taxation on the memory of the average students and makes the subject appear dull, difficult and uninteresting to them.

All the above considerations were kept in mind while writing this book. Ours is a modest but sincere attempt to write a book which, we earnestly hope, will be of real help to the general students in their aim of acquiring a working knowledge of the fundamental principles of general chemistry and to be able to apply this knowledge to work out the descriptive chemistry of the elements and their compounds.

The book is divided into Part I and Part II. Part I begins with an "Introduction" which summarises the more important topics of general chemistry included in the Higher Secondary course and serves as a logical link between the Higher Secondary course and the new degree syllabi. The rest of the part I includes the important fundamental principles of general chemistry, spanning chapters I—VII. The discussions of these principles are illustrated with adequate diagrams and figures, and abound in relevant examples from inorganic chemistry along with numerical examples wherever essential. The remaining portion of part I deals with the chemistry of the periodic groups O, IA, IB, IIA, IIB and IIIA. The **Appendix** of this part deals with numerical problems and includes both worked out examples and exercises to be worked out by the students.

The part II of this book will contain the descriptive inorganic chemistry of the elements of the rest of the periodic groups included in the syllabi, written on the basis of their electronic configuration, position in the periodic table, and the influence of the physical factors like atomic and ionic radii, ionization potential and electron affinity, electronegativity, the nature of the bonding involved etc.

We sincerely hope that this book will meet the requirements of the students and teachers, generated as a result of the introduction of the new syllabi. We had to write this book rather hurriedly, as a result of which some minor errors and inadequacies might have crept in and for which the responsibility is entirely ours.

All criticisms and suggestions about this book will be thankfully received and gratefully acknowledged.

Calcutta,
15th August,
1979

**AUTHORS**

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## APPENDIX

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CHAPTER I

# ATOMIC STRUCTURE

## *The Outer Sphere of the Atom*

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The atomic theory is the basis on which our entire understanding of chemical phenomena rests. In the late 18th century and the beginning of the 19th century, the foundations of the modern atomic theory were laid down as a result of the attempt to understand the chemical properties of matter. On the basis of the rather crude experimental data available to him, the English school teacher, John Dalton, proposed his famous **atomic hypothesis** (which later became **atomic theory** on being substantiated by subsequent works), according to which the existence of **atoms** was accepted as fact. Chemistry rests largely on this theory which can clearly explain the quantitative laws of chemical combination. **The Daltonian atomic theory** recognises that all matter are composed of tiny, indivisible and indestructible particles called atoms. But, to-day the atom is no longer considered as the smallest particle of matter and is not considered indivisible. It has been proved experimentally that it consists of smaller sub-atomic particles like the **electron,** the **proton,** the **neutron** *etc*. arranged in a complex but systematic pattern, the unfolding of which is the major object of the modern theory of atomic structure.

Of the next steps in the gradual development of the modern theory of atomic structure in the post-Daltonian era, the following are of great importance :

1. The discovery of the electrical nature of matter and the atomic nature of electricity itself.

2. The discovery that the atom consists of a positively charged nucleus surrounded by the negatively charged **electrons.**

3. The discovery of the mechanical laws which govern the motion of the electrons in atoms.

From the results of his works on the electrolysis of aqueous solutions of chemical compounds, Faraday, in 1833, put forward his two famous **laws of electrolysis** which are one of the corner-stones of modern physical sciences. Faraday realised that electricity is carried through the solution by charged particles called **ions.** His second law led to the conclusion that one gram-equivalent of any element is dissolved from or deposited on an electrode by 96500 coulombs or one Faraday (F) of electricity. Since one gram-equivalent of any element is discharged by one Faraday of electricity, for any atom of valency *n*, one gram-atom of the element will carry *n*F Faraday of electricity, where *n* is always an integer. As the number of individual atoms in one gram-atom of any element is the same, *viz.* $N_0$, ($N_0$= Avogadro number=$6{\cdot}03\times10^{23}$), the ionic charges of all elements are integral multiples of the quantity $F/N_0$. This indicates that electricity itself is also atomic in nature. Unfortunately, the actual significance of this conclusion could be recognised by G.J. Johnson Stoney only after a lapse of 41 years in 1874, and he suggested the name **'electron'** for the fundamental unit of electricity of either kind, positive or negative. But, it was only in 1897 that a firm experimental verification of the existence and properties of electrons were achieved during the study of conduction of electricity through rarefied gases.

**Cathode rays and the discovery of the electron.**

A stout glass tube, containing a gas, (say, nitrogen) is fitted with two fused-in electrodes (Fig. 1.1). O is an outlet through which the enclosed gas can be pumped out. To the two electrodes, high potential difference of the order of 10,000 volts can be applied, using an induction coil as the source. At first, the whole tube glows on the passage of electricity. As the pump is worked and the pressure inside the tube falls to $10^{-4}$ to $10^{-5}$ cm. of mercury, the illumination disappears and a fluorescent glow appears on the wall of the discharge tube opposite to the cathode. This glow is due to the impact of certain rays emanating from the cathode which were named **cathode rays.** The following properties of the cathode rays established their identities as negatively charged particles :

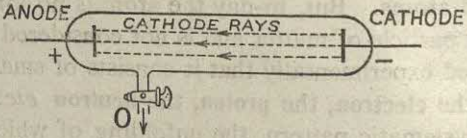

Fig. 1.1

1. They carry considerable amount of kinetic energy and hence are composed of particles having some mass.

2. When the cathode rays are allowed to strike the knob of a gold leaf electroscope charged with positive electricity, it gets discharged, indicating the negative nature of the cathode ray particles. Also

the rays are deflected by a magnetic field or an electric field in a direction corresponding to the presence of negatively charged particles.

The only reasonable explanation of these experimental facts is that, cathode rays consist of fast moving negatively charged particles which are identified later as **electrons** of Johnson Stoney. It is also found that **the cathode ray particles are independent of the material of the electrodes and the nature of the enclosed gas.**

**Determination of specific charge (*e*/*m*) of the electron.**

In 1898, the famous physicist Sir J. J. Thomson designed and carried out an experiment which enabled him to determine the speed of the cathode ray particles or electrons and to evaluate its *e*/*m* value, *i.e.*, charge/mass ratio. His apparatus is shown in fig. 1.2.

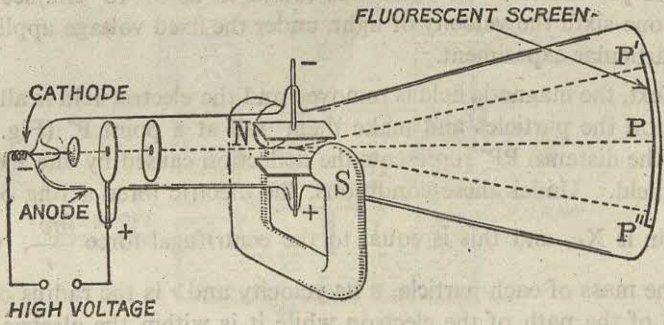

Fig. 1.2

The apparatus is a modified cathode ray tube. Cathode rays are emitted from the cathode and are allowed to pass through the perforations in the anode and another metal plate with a narrow slit and to fall on a point (P) of the fluorescent screen or photographic plate placed at the right-hand end of the cathode ray tube.

The cathode rays affect photographic plate just like the X-rays or ordinary light rays. An electromagnet N S was placed near the tube in a manner so that when the magnetic field is switched on, the lines of forces are perpendicular to the direction of movement of the cathode rays. Two plates were sealed inside the tube by means of which a strong electric field could be applied in a direction perpendicular to the directions of both the cathode rays and the magnetic field. When the magnetic field is applied, the cathode rays will bend and will fall on the point P′ instead of P. Now, for this fixed value of the strength of the magnetic field, the strength of the electric field is gradually increased until the beam comes back to the central position P at which it would have struck in the absence of the magnetic field. Thus, under the experimental conditions, the force on the cathode ray particles or electrons due to the magnetic field, $Hev$, is equal to the force due to the electric field $Xe$, where H and X are the strengths of magnetic and electric fields respectively, $e$ is the charge of an electron and $v$ its velocity.

$$\text{Thus,}\quad Hev = Xe$$

$$\text{or,}\quad v = \frac{X}{H} \quad \cdots\cdots\ (1.1)$$

The velocity of the electron can be calculated from the magnitudes of the magnetic field H and the electric field X. If X, $e$ and H are expressed in electromagnetic units, the velocity has the units of centemeters per second. Its value was found to be $5 \times 10^9$ cm./sec. *i.e.*, about one-sixth the velocity of light, under the fixed voltage applied in that particular experiment.

Next, the magnetic field is removed and the electric field is allowed to act on the particles and make them fall at a point P″ (Fig. 1.2). Thus, the distance PP″ represents the deflection caused by the electrostatic field. Under these conditions, the electric force acting on the electron is $Xe$, and this is equal to the centrifugal force $\frac{mv^2}{r}$, where $m$ is the mass of each particle, $v$ its velocity and $r$ is the radius of curvature of the path of the electron while it is within the electric field.

$$\text{Thus,}\quad Xe = \frac{mv^2}{r} \quad \cdots\cdots\cdots\cdots\ (1.2)$$

Putting the value of $v$ from eqn. (1.1.) we get,

$$X.e = \frac{m}{r}\left(\frac{X}{H}\right)^2$$

$$\text{or,}\quad e/m = \frac{X}{H^2 r} \quad \cdots\cdots\cdots\ (1.3)$$

$r$ can be easily measured from the instrumental set-up (Fig. 1.2).

The $e/m$ value, found by Thomson, was $1{\cdot}7 \times 10^7$ e.m.u./gm. or $5{\cdot}1 \times 10^{17}$ e.s.u./gm. **This value was found to be independent of the nature of the gas inside the cathode ray tube and of the materials of the cathode.**

**Determination of the electronic charge, 'e'.**

After the determination of $e/m$ of the electron, the problems of determining individually its charge '$e$' and its mass '$m$' automatically presented themselves. It is to be noted that since the value of $e/m$ is known, determination of the value of either '$e$' or of '$m$' will lead to the evaluation of either of the two quantities.

Of the numerous workers who attempted to measure the charge on the electron, R.A. Millikan was most successful. It was known at that time that electrically charged ions act as nuclei for the condensation of water vapour, forming droplets of cloud which can be viewed by a powerful telescope eyepiece as tiny specks of light in a strongly illuminated field. A sketch of the apparatus used by Millikan is given in Fig. 1.3.

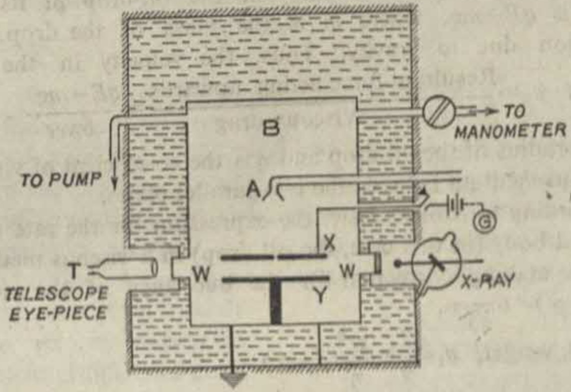

Fig. 1.3

By means of his celebrated experiments, Millikan proved that all electric charges are integral multiples of one definitely elementary unit whose value is $4{\cdot}80 \times 10^{-10}$ e.s.u. or $1{\cdot}6 \times 10^{-19}$ coulombs.

In an almost evacuated vessel B, minute spherical oil-drops from an atomizer A are led into the observation chamber. At the lower portion of this chamber are placed two accurately parallel plates X and Y, to which a high potential difference (of the order of 5000 volts) can be applied. In course of time, one oil-drop enters the space between the two plates X and Y through the aperture in the upper plate. In the absence of the electric field, the oil-drop is under the influence of gravity only, and falls down towards the lower plate which is earthed. With the help of a telescope and stop-watch, the constant downward velocity $v_1$ of the drop is measured. Now, a narrow beam of X-rays is allowed to fall on the gas between the two plates. This ionizes some gas molecules which are absorbed by the oil-drop. When the oil-drop almost touches the lower plate Y, the upper plate is connected to an induction coil. As a result, the oil-drop now starts to rise upwards and the constant upward velocity ($v_2$) of the oil-drop is measured as before. When the droplet almost touches the upper plate X, the electric field is switched off and the drop is again allowed to fall under gravity until it almost reaches the lower plate. Then the field is switched on again and the drop moves up. In this way, the same oil-drop is moved up and down for a large number of times.

If the oil-drop contains an amount of charge '$q$' and the magnitude of the electric field be E, the electrical force acting upon the oil-drop causing it to move upward is $q$E. Since the force of gravity is acting downwards on the oil-drop simultaneously with the electric field, the resultant force acting on the oil-drop in its upward journey is $qE-mg$, where $m$ is the mass of the drop and $g$ is acceleration due to gravity. Thus, the velocity in the upward direction, $v_2 = \frac{\text{Resultant force acting upwards}}{\text{Viscous drag}} = \frac{qE-mg}{6\pi\eta r}$ .... (1.4)

where $r$=radius of the oil-drop and $\eta$ is the co-efficient of viscosity of the gaseous medium between the two parallel plates.

According to Stoke's Law, the expression for the rate of fall of a spherical body (in this case, the oil-drop) in a viscous medium (say air), after making correction for the buoyancy of the medium, is

$\frac{4}{3}\pi r^3 g(\rho-\rho') = 6\pi\eta r v_1$ ....... (1.5)

From this, we get, $v_1 = \frac{2}{9}\times\frac{gr^2}{\eta}(\rho-\rho')$

and $r = \left[\frac{9}{2}\times\frac{\eta v_1}{g(\rho-\rho')}\right]^{\frac{1}{2}}$ ...... (1.6)

Here $\rho$=density of the oil-drop and $\rho'$=density of the gaseous medium between the two plates, while $r$, and $\eta$ have significances as stated before. The value of $v_1$ is determined experimentally as stated and the values of $\rho$, $\rho'$ and $\eta$ can be easily obtained by standard methods. Putting all these values in equation (1.6), the value of $r$ is obtained and from this value of $r$, the mass of the oil-drop '$m$' can be calculated. When the values of $r$,$m$ and $\eta$ are put in eqn. (1.4), along with the experimental values of $v_2$ and E, $q$ can be easily calculated. From the analysis of the results obtained, it was found that the droplet falling under gravity always takes the same time to fall to the lower plate from the upper plate. But, while moving upward, the droplet required different times on different journeys. It is quite obvious that the reason behind is that the droplet must have picked up more charges on its way, as a result of which different values of $q$ are found in different upward journeys. Millikan found that $q$ was always an integral multiple of $4{\cdot}8\times10^{-10}$ e.s.u. This result definitely shows that electricity is particulate in nature and the fundamental unit of electric charge, or the electronic charge is $4{\cdot}8\times10^{-10}$ e.s.u.

Using this value of $e$ and the value of $e/m$ determined before, the mass of the electron can be obtained.

$$e/m=5{\cdot}27\times10^{17}\text{ e.s.u./gm.}$$
$$\text{and } e=4{\cdot}8\times10^{-10}\text{ e.s.u.}$$
$$\therefore\quad m=\frac{4{\cdot}8\times10^{-10}}{5{\cdot}27\times10^{17}}$$
$$=9{\cdot}1\times10^{-28}\text{ gms.}$$

This mass is $\frac{1}{1837}$th of the mass of a hydrogen atom.

**Positive rays.**

The atoms of all elements are electrically neutral. The fact that, on ionization atoms yield electrons as a stream of cathode ray particles suggests that, stream of positively charged particles is also formed in the process. In 1886, Goldstein discovered such positive rays by using a perforated cathode, when the rays of the positively charged particles streamed out through the perforations or canals in the cathode (figure 1.4). These were named as **canal rays** or **positive rays.** As in the case of cathode rays, the velocity (depending on the potential difference used) and the $e/m$ values of the positive ray particles were determined, using the same type of apparatus. It was found that both the velocity and the $e/m$ ratio were much less than that of the electron, and the values of $e/m$ were dependent on the nature of the gas inside the discharge tube. It decreased with the increase in the atomic weight of the gas. Thus, the $e/m$ value was highest when the lightest gas hydrogen is present in the discharge tube. Thus, with hydrogen, the smallest positively charged particle was obtained and the name 'proton' was given to it.

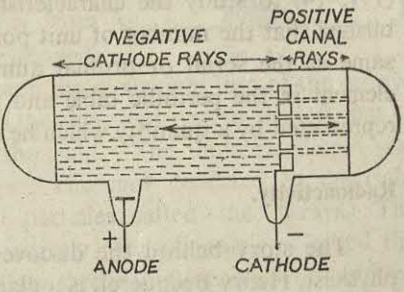

Fig. 1.4

**X-rays.**

In 1895, Röntgen discovered that a new kind of radiation is produced when a beam of cathode rays is allowed to strike a solid target (Fig. 1.5). It produced a greenish fluorescence on the walls of the glass tube at the point through which it emerged out.

This radiation affected photographic plates, could penetrate thick black paper or thin metal foils and caused ionization in gases. The name **X-rays** was given to this new radiation. The X-rays travel in a straight line and could not be deflected by electric or magnetic fields, and hence were not charged particles. Later on, it was found that they were electromagnetic radiations of very short wave length ($\lambda = 10^{-8}$ to $10^{-11}$ cm.). The X-rays produced fluorescence on many substances on which they were allowed to fall and many scientists at that time thought that there was a close relation between X-rays and fluorescence. It is an attempt to find out whether X-rays are emitted during the fluorescence of a uranium compound that led to the accidental discovery of the entirely new phenomenon of **Radioactivity**. Further, the use of X-rays by Mosely (1913-14) to study the characteristic X-ray spectra of elements established that the number of unit positive charges on the nucleus is the same as the serial or ordinal number of the place occupied by the element in the periodic table and that both these numbers could be represented by a quantity which he called **atomic number.**

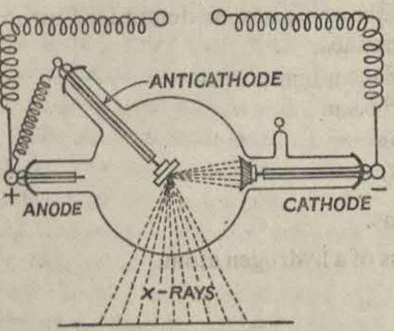

Fig. 1.5

### Radioactivity.

The story behind the discovery of radioactivity by the French physicist, Henry Becquerel, is a glaring example of accidental circumstances helping a scientifically prepared mind to find out the truth, even through the cloud of a crudely designed experiment. We shall deal with the details of the subject-matter of radioactivity in a later chapter.

In 1896, Becquerel discovered that, certain uranium compounds emit a peculiar penetrating type of radiation hitherto unknown. These radiations, like X-rays, could pass through thick black paper and affect photographic plates. Becquerel named the phenomenon **Radioactivity** and the elements responsible for this were called radioactive elements or simply radioelements. The process of emitting radioactive radiations became known as the process of radioactive disintegration. The rays produced ionization in gases through which they passed. In 1898, Mme. Curie and her husband, Pierre Curie, isolated two new elements, polonium and radium, from the uranium ore, pitchblende. Within a few years, thorium and actinium were found to be radioactive. It was clearly recognised that the phenomenon of radioactivity was an atomic phenomenon, as the products of radioactive disintegration were entirely different from the parents. It was also established that the phenomenon of radioactivity was independent of the physical and chemical nature of the element to which it is due.

**α, β and γ rays.**

When radioactive radiations from a radioelement are allowed to pass through a strong magnetic or electric field, they are split up into rays of three different characteristics as shown in Fig. 1.6. A narrow beam of radioactive radiations is obtained by placing a small amount of a radioactive substance in the deep groove of a block of lead. A photographic plate (P) is placed at some distance above the lead block and the whole arrangement si placed in an evacuated vessel. A magnetic field is applied at right angles to the plane of the diagram and directed away from the reader. When the plate is developed, three distinct spots are found, one in direct straight line of the groove in the lead block, one deflected to the right and one to the left, but to a lesser extent than the spot on the right. The undeviated spot was obviously caused by neutral rays. The spot deflected to the right were due to negatively charged particles called the **β-rays.** The spot on the left is caused by positively charged particles called the **α-rays.** It had been shown that all the three radiations were not emitted simultaneously by all radioelements. Some elements emit α-rays, others β-rays, while γ-rays sometimes accompany either the α-or the β-rays. The activity of a given material is independent of its physical state of occurrence and also of its state of chemical combination.

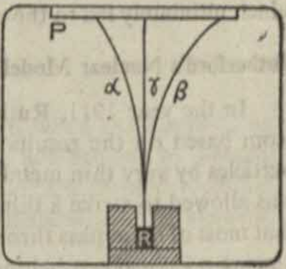

Fig. 1.6

From the value of *e*/*m* of the β-particles and also from some other properties of these particles, they were identified with fast moving electrons. Ernest Rutherford made an ingeneous experiment to prove that the α-particles are helium atoms carrying two units of positive charge. Thus, it was conclusively proved that atoms contained both positively and negatively charged particles. With the establishment of the particulate nature of electricity, the recognition of the electron as a fundamental constituent of all atoms, determination of its charge and mass and the conclusive proof from the positive ray analysis and the phenomenon of radioactivity that atoms contained both positively and negatively charged particles, an intensive research for ascertaining the more detailed picture of the atom began. The first attempt to plan a model of the atom was made by J. J. Thomson, who proposed that the atom is a sphere of positive electricity of uniform density with a radius of about $10^{-8}$ cm. and the electrons are embedded in this sphere of positive electricity. For the sake of electroneutrality, the number of electrons is equal to the number of positive charges. With this model, Thomson tried to explain, among other things, the periodic properties of elements and even tried to develop a theory of chemical bonding. But, it was found to be almost totally inadequate, particularly in explaining the **scattering of α-particles** by thin metal-foils, which ultimately led to the concept of the **nuclear atom.**

### Rutherford's Nuclear Model of the Atom.

In the year 1911, Rutherford proposed the nuclear model of the atom based on the results of his experiments on the scattering of α-particles by very thin metal-foils. When a narrow beam of α-particles was allowed to strike a thin metal-foil (0·0005 cm. thick), it was found that most of them pass through the metal-foil and are easily detected by placing a ZnS-screen behind the foil, on which each particle produces a minute flash. The angular distribution of the scattered α-particles were thus observed and it was found that most of the particles pass through the metal-foil either undeviated or they undergo a very small deflection from the original direction. A very few (say, 1 in 20,000) are scattered at large angles upto 180° (figure 1.7). Rutherford suggested that the deflections through large angles could be caused by a single encounter with an atom than by multiple scattering. Since the α-particle is a doubly charged helium atom, the experimental results can be explained by assuming that, most of the mass and all the positive charge of the atom is concentrated into a tiny particle which Rutherford called the **atomic nucleus.** The salient features of Rutherfords nuclear model of the atom is as follows :

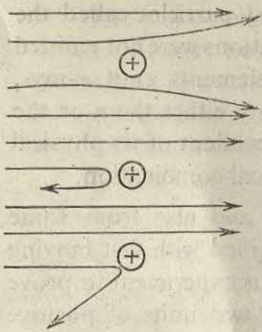

Fig. 1.7

1. Most of the mass of an atom is concentrated at a very minute nucleus placed at the centre of the atom. The radius of the atom is of the order of $10^{-8}$ cm., while that of the nucleus is in the region of $10^{-13}$ cm.

2. All the positive charge of an atom is present in the nucleus. The total positive charge in the nucleus of the atom may be represented as *Ze*, where *e* is the unit positive charge, equal in magnitude to the charge of an electron, but of opposite sign, and Z is the number of such positive charges present in the nucleus.

3. Far away from the nucleus, there are Z number of extra-nuclear electrons, so as to make the atom electrically neutral.

4. These electrons revolve round the nucleus with such velocity that the centrifugal force of circular motion is exactly balanced by the centripetal force due to the attraction of the positive nucleus on the electrons. *The whole atom resembles the solar system with the nucleus taking the position of the sun while the electrons revolve round it like the planets.*

**Atomic spectra : Their discrete nature.**

It had long been known at that time that, when the atoms of an element in the gaseous state, say hydrogen, are excited by passing electric discharge through the gas and the resultant emitted radiation is passed through a prism, a line spectrum, characteristic of the element, is observed (Fig. 1.8).

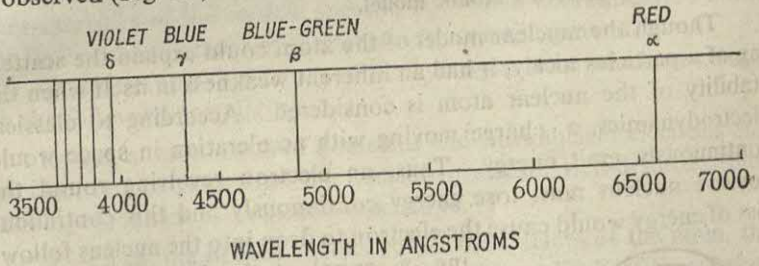

Fig. 1.8

In the line spectrum (emission spectrum) of hydrogen (shown above), the frequencies of the different spectral lines can be related by a simple equation. Such equations are generally expressed in terms of *wave numbers** ($\bar{\nu}$) instead of wavelength or frequency ($\nu$) of the radiation in question. Thus, the wave numbers of different lines in the emission spectrum of hydrogen can be represented by the equation :

---

*The frequency of a wave is represented by $\nu = c/\lambda$($\lambda$ is the wavelength and $c$ is the velocity of the wave per second) and gives the number of vibrations per second. The wave number $\bar{\nu}$ is the number of vibrations per centimetre and is given by $\frac{1}{\lambda}$, where $\lambda$ is the legnth of the wave in centimetre. Thus, $\bar{\nu} = \frac{\nu}{c}$.

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \ldots\ldots\ldots\ldots (1.7)$$

where $n_1$ and $n_2$ are integers and $R$ is a constant known as **Rydberg constant.**

It was observed further that this line spectrum of hydrogn consisted of several groups of closely spaced lines each of which is termed as a **series.** The equation (1.7) can be written as $\bar{\nu} = \frac{R}{n_1^2} - \frac{R}{n_2^2}$, in which each of $\frac{R}{n_1^2}$ and $\frac{R}{n_2^2}$ is called a term and each and every spectral line of any one series is represented by a difference of two such terms. This is known as the **Ritz combination principle.**

Though the discrete character of the emission spectrum could not be explained at that time, the regularity of the occurrence of the spectral lines indicated that the excited hydrogen atom emitted energy **discontinuously.** If it had emitted energy continuously, a continuous band of the emitted energy would have been observed instead of discrete lines.

## Defects of Rutherford's atomic model.

Though the nuclear model of the atom could explain the scattering of $\alpha$-particles nicely, it had an inherent weakness in itself when the stability of the nuclear atom is considered. According to classical electrodynamics, a charge moving with acceleration in space would continuously emit energy. Thus, an electron revolving round the positive nucleus must lose energy continuously and this continuous loss of energy would cause the electron to drop into the nucleus following a spiral path (Fig. 1.9) just as a satellite returns to earth as it loses energy on account of friction with the atmosphere. Thus, the separated nucleus-extranuclear electron system will be unstable. Further, such a model could not explain the discontinuous nature of the emission spectra of the gaseous atoms observed experimentally.

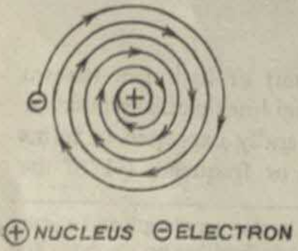

Fig. 1.9

## Application of Quantum theory of radiation to atomic spectra.

The failure of Rutherford's nuclear model of the atom to explain the stability of the atom and its inability to explain the origin of the line spectrum of gaseous atoms exposed the inadequacy of classical mechanics when applied to atomic phenomena. Even earlier, it was found that classical mechanics failed to explain the dependence of the intensity of the radiant energy emitted by a '*black body*' on the wavelength of the radiation. To explain this phenomenon of '*black body radiation*', a new concept had to be developed, which was entirely opposed to the ideas of classical physics. Thus, in 1901, Planck proposed his revolutionary **quantum theory of radiation.** According to Planck, radiant energy emitted by a body is not continuous in character, but it is emitted by discrete packets or *quanta*. Such a quantum or unit of radiant energy is termed a *photon*. Planck showed mathematically that the energy of a photon is directly proportional to its frequency : $E \propto \nu$, or $E = h\nu$, where $h$ is called the Planck's constant and it has the value of $6{\cdot}627 \times 10^{-27}$ erg-sec. .. .. (1.8)

### The Bohr theory of atomic spectra and atomic structure.

In 1913, the celebrated Danish physicist, Niels Bohr, applied the quantum theory of radiation to Rutherford's model of nuclear atom and developed a new theory of the constitution of hydrogen atom which overcame the defects of Rutherford's theory and accounted for many characteristics of the atomic spectra, and it laid the foundation stone for further development of the atomic structure in general.

Bohr developed his theory of the hydrogen atom which was based on the following postulates :

1. An atom consists of a nucleus and extranuclear electrons and the electrons move around the nucleus in certain well-defined orbits, obeying all the laws of classical mechanics.

2. Of all the possible orbits round the nucleus of the atom, the electron can rotate only in certain stable orbits. Each of these orbits is associated with a definite amount of energy which increases as one moves from the nucleus outwards. So long as an electron remains in such an orbit, it will neither radiate nor absorb energy. Such a stable orbit is called a **stationary orbit.**

3. A stationary orbit is defined to be such an orbit in which the angular momentum of an electron is an integral multiple of $h/2\pi$. In other words, in a stationary orbit, the angular momentum is always quantised and is given by the expression, $mvr = n \times \frac{h}{2\pi}$, where '$n$' is an integer with values 1,2,3 etc. and is known as the principal quantum number. It stands for the serial number of the allowed orbits.

4. Each of such stationary orbits or states is circular in nature.

5. Though an electron in one of the stationary orbits does not absorb or radiate energy, it can jump from one stationary orbit to other orbits of lower or higher energy. In such a process, if it jumps from an energy state $E_1$ to another energy state $E_2$, it will radiate or absorb an amount of energy $h\nu$, which is equal to the difference in the energy of the two stationary states, $E_2 \sim E_1 = h\nu$ .. .. .. .. ..(1.9) When $E_2$ is the energy of the electron in the higher energy stationary state and $E_1$ is the energy of the electron in the lower energy stationary state, energy will be radiated and $\nu$ will be the frequency of the radiation emitted.

When the electron jumps from a lower to a higher energy orbit it absorbs an amount of energy, obeying the same relation.

Expressions for the energies of the electrons in the stationary states can be easily calculated using Bohr's postulates. Fig. 1.10 represents Bohr's atomic model and the relevant drawings for the above calculations.

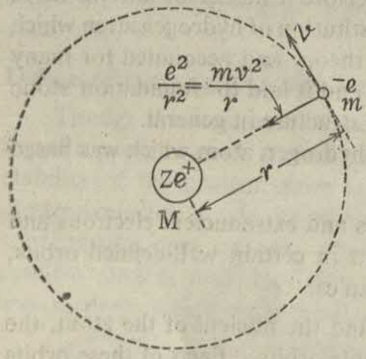

Fig. 1.10

The positively charged nucleus has a mass of M and Z is the number of units of elementary charge $e$ on the atomic nucleus. The mass of the electron is $m$ and $r$ is the radius of the stationary orbit in which the electron revolves with a linear velocity $v$. The positively charged nucleus attracts the negative electron with a force according to Coulomb's principle, $F = \frac{Ze^2}{r^2}$ .. .. (1.10)

Again, the centrifugal force experienced by the moving electron is given by $\frac{mv^2}{r}$. For the stability of the system, this centrifugal force must equal the coulombic force of attraction, *i.e.*,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

$$\text{or, } v^2 = \frac{Ze^2}{rm} \quad \cdots \cdots \cdots \quad (1.11)$$

From the second postulate of Bohr's theory, we have,

$mvr = n\dfrac{h}{2\pi}$, where $n$ is an integer which is known as the **principal quantum number** and can have values of 1,2,3. . . .

$$\text{or,}\quad m^2v^2r^2 = \frac{n^2h^2}{4\pi^2}$$

$$\therefore\quad v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \quad \ldots\ \ldots\ \ldots \quad (1.12)$$

From equation 1.11 and 1.12 we get,

$$\frac{Ze^2}{rm} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

$$\text{or,}\quad r = \frac{n^2h^2}{4\pi^2Ze^2m} \quad \ldots\ \ldots\ \ldots \quad (1.13)$$

$$= n^2\left[\frac{h^2}{4\pi^2mZe^2}\right] \quad \ldots\ \ldots\ \ldots (1.14)$$

Here all the quantities in parenthesis in eqn. 1.14 are constant for a particular atom, except '$n$' which can have values of 1, 2, 3. . . . . . Thus, the radius of a particular stationary orbit can be calculated by putting appropriate value of the **principal quantum number** $n$ in eqn. 1.14. The value of $n$ determines the size of the stationary orbit. Higher the value of $n$, larger is the distance of the orbit from the nucleus. Each value of $n$ represents an energy shell and the letters K,L,M,N,O. . . . . . are used to denote electron-shells having the principal quantum numbers of 1, 2, 3, 4, 5 etc. The orbit, corresponding to $n=1$, has the least energy and consequently is the stablest. This is called the **ground state** of the hydrogen atom.

Now, the total energy E of the electron is the sum total of its kinetic energy, $\frac{1}{2}mv^2$, and its potential energy, $-\dfrac{Ze^2}{r}$.

Thus, $E = \frac{1}{2}mv^2 + (-Ze^2/r)$

Putting $mv^2 = \dfrac{Ze^2}{r}$ we get,

$$E = \frac{1}{2}\frac{Ze^2}{r} - \frac{Ze^2}{r} = -\frac{1}{2}\frac{Ze^2}{r} \quad \ldots\ \ldots\ \ldots \quad (1.15)$$

Substituting the value of $r$ from eqn (1.14) into eqn. (1.15) we get,

$$E = -\frac{1}{2}\,\frac{Ze^2 \times 4\pi^2 mZe^2}{n^2h^2}$$

$$= -\frac{2\pi^2 mZ^2e^4}{n^2h^2} = -\frac{2\pi^2 mZ^2e^4}{h^2} \times \frac{1}{n^2} \quad \ldots \ldots \quad (1.16)$$

$$[n=1,2,3,\ldots\ldots\ldots]$$

Thus, higher the value of principal quantum number $n$, greater is the energy of the corresponding stationary orbit.

Putting the appropriate value of $n$ in eqn. (1.16), the energy of a particular orbit can be obtained. This expression shows that only certain energies are allowed to an electron. The energy of a free electron separated from the nucleus by an infinite distance is taken to be zero, and since the energy of an electron in an atom is less than that of a free electron, the energy of the electron in any stationary orbit is negative. The lowest energy level of the atom corresponds to $n=1$. When $n=\infty$, E becomes zero, and this corresponds to an ionized atom from which the electron is removed. The energy radiated by an electron in jumping from a state of energy $E_2$ to a state of lesser energy $E_1$ is given, according to Bohr's 4th postulate, as

$$h\nu = E_2 - E_1 = -\frac{2\pi^2 mZ^2e^4}{h^2}\cdot\frac{1}{n_2^2} + \frac{2\pi^2 mZ^2e^4}{h^2}\cdot\frac{1}{n_1^2}$$

$$= \frac{2\pi^2 mZ^2e^4}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \ldots \ldots \quad (1.17)$$

$$\text{or,} \quad \nu = \frac{2\pi^2 mZ^2e^4}{h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \ldots \ldots \quad (1.18)$$

Replacing frequency ($\nu$) by wave number $\bar{\nu}$ ($\bar{\nu}=\nu/c$),

$$\text{we get,} \quad \bar{\nu} = \frac{2\pi^2 mZ^2e^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \ldots \ldots \ldots \quad (1.19)$$

$$= R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \ldots \ldots \ldots \quad (1.20)$$

Here $R = \frac{2\pi^2 mZ^2e^4}{ch^3}$ = Rydberg constant, and for hydrogen atom ($Z=1$) it has a value of 109737 cm.$^{-1}$. Thus, the frequency of the radiation emitted when the electron jumps from one stationary orbit to another, can be easily calculated from eqn. 1.18 and 1.20. For the hydrogen atom $Z=1$, and if we consider the electron to be in the ground state ($n=1$), the radius of the atom can easily be calculated to be $r = 0{\cdot}529 \times 10^{-8}$ cm. or $0{\cdot}529\,\mathring{A}$. In the same manner the radius of different

Bohr orbits of hydrogen can be calculated by putting $Z=1$ and $n=1$, 2, 3 etc. in eqn. 1.13. Similarly, by putting $Z=1$ and appropriate values of $n$ in the expression (1.16) and also in either eqn. (1.18) or (1.19), the energy of the electron in any stationary orbit and the frequency and the wave number of the radiation emitted when the electron jumps from a higher energy state ($E_2$) to a lower energy state ($E_1$) can be calculated.

It is now possible to account for the occurrence of the different series of spectral lines in the spectrum of hydrogen given in Fig. 1.11. When an electron jumps down to the orbit specified by the principal quantum number $n=1$ from any of the outer orbits with $n=2,3,4,5,\ldots\ldots$, the lines of the **Lyman series** are produced. In a similar manner, **Balmer, Paschen, Brackett** and **Pfund** series are formed when electrons jumps to orbits having $n=2,3,4$, and 5 respectively from outer orbits.

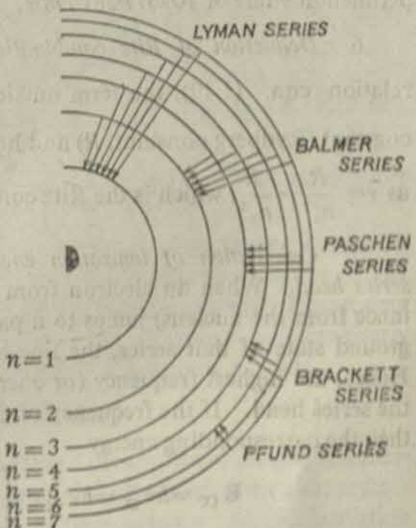

Fig. 1.11

**Achievements of Bohr's theory.**

1. Bohr's theory could explain the hydrogen spectrum and also the spectra of other hydrogen-like one-electron systems such as $He^+$ $Li^{+2}$, $Be^{+3}$ *etc.*

2. It was successful in calculating the radius of the various stationary orbits [eqn. (1.13)]. The calculated radius of the first Bohr orbit of the hydrogen atom was in agreement with experimental observation.

3. Bohr's theory introduced the concept of quantum numbers (principal quantum number) .for the first time. The electronic transitions predicted and their characteristic features explained by the theory were in close agreement with experimental findings.

4. *Explanation of the existence of spectral series in the spectrum of hydrogen.* Using different values of $n_1$ (1, 2, 3 etc.), the frequency-relation [eqn. (1.19) or (1.20)] explains the formation of spectral series

in the spectrum of hydrogen. This predicts a completely different series for each value assigned to $n_1$. Thus, for values of $n_1=1, 2, 3, 4$ and 5 respectively, the Lyman series, the Balmer series, the Paschen series, the Brackett series and the Pfund series are generated.

5. *Calculation of the Rydberg constant.* The value of Rydberg constant, R, can be calculated from the Bohr-relation [eqn. (1.20)].

$$R=\frac{2\pi^2Z^2e^4m}{ch^3}.$$

The calculated value $R=109400\ cm^{-1}$ agrees fairly well with the experimental value of 109677·581 $cm^{-1}$.

6. *Deduction of Ritz combination principle.* In the frequency-relation eqn. (1.19), the term outside the bracket, *i.e.* $\frac{2\pi^2Z^2e^4m}{ch^3}$ is constant (Rydberg constant, $R$) and hence the eqn. 1.19 can be written as $\bar{\nu}=\frac{R}{n_1^2}-\frac{R}{n_2^2}$, which is the Ritz combination principle.

7. *Calculation of ionization energy from the frequency of the series head.* When an electron from $n=\propto$(*i.e.* from an infinite distance from the nucleus) jumps to a particular orbit that represent the ground state of that series, the line at that series head is generated. Hence, the highest frequency (or energy) line of a particular series is the series head. If the frequency of this radiation be denoted by $\nu_\propto$, then the corresponding energy

$$E_\propto=h\nu_\propto=h\bar{\nu}_\propto c\ \left[\because\ \frac{\nu}{c}=\bar{\nu}\right]$$

Again, from eqn. (1.20)

$$\nu_\propto=R\left[\frac{1}{n_1^2}-\frac{1}{\propto^2}\right]\ \text{(here, } n_2=\propto)$$

$$=R\times\frac{1}{n_1^2}.$$

Thus, if we know the value of $n_1$ corresponding to the ground state of the electron, $\nu_\propto$ and hence $E_{\propto\rightarrow n_1}$ can be calculated. Again, ionization energy is defined to be the amount of energy necessary to remove an electron from an atom to an infinite distance. Thus, the ionization energy (or potential) is numerically equal to the energy required to generate the series head. Hence, the ionization energy (or potential) of an electron in a particular orbit can easily be calculated.

### Limitations of Bohr's theory.

With the introduction of new high-resolution spectroscopes, the spectra of hydrogen and other hydrogen-like atoms and ions showed some new characteristic features which could not be explained by Bohr's theory, and thus exposed its following defects :

1. The theory could not explain the spectra of systems containing two or more electrons.

2. When the atom emitting radiation is placed in a magnetic field, some of the lines are split into more than one components (**Zeeman effect**). The same thing happened when the source is placed in an electric field (**Stark effect**). Such splitting of single lines into a number of components and the resultant additional lines are known as fine structure lines. Bohr's theory could not explain the existence of such fine structure lines.

3. Bohr's model was a two dimensional one, while an atom is actually three dimensional.

4. Last, but not the least, is the fact that by precisely defining the radius of the atomic orbit and the angular momentum of the electron revolving in it, Bohr's theory violated **Heisenberg's Uncertainty Principle** which states that, it is impossible to define simultaneously the position and momentum of a moving sub-atomic particle.

### Sommerfeld's modification of Bohr's model.

In order to explain the finer details of the spectra of atoms, Sommerfeld (1915) proposed the following modifications of Bohr's theory :

(i) *Introduction of the concept of reduced mass.* In the derivation of the energy of a stationery orbit, $E_n = -\dfrac{2\pi^2 Z^2 e^4 m}{h^2 n^2}$, Bohr assumed that the electron of mass '*m*' rotates around a stationary (static) nucleus. But, it can be shown from elementary principles of classical mechanics that the nucleus, if not of infinite mass, cannot be considered to remain stationary. Whenever a particle of finite mass (here, the electron of mass '*m*') moves in a circle about another particle also of finite mass (here, the nucleus of mass 'M'), the latter particle must also move in a circle about the common centre of mass ('*c*') (Fig. 1.12). Thus, in order

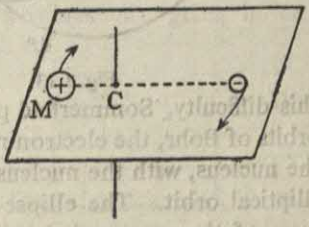

Fig. 1.12

to get the correct value of $E_n$, the motion of the nucleus must also be taken into consideration. The expression for the energy of the $n$th stationary orbit would thus assume the form

$$E_n = \frac{2\pi^2 Z^2 e^4}{n^2 h^2} \times \mu,$$

where μ is known as the reduced mass of the electron which replaces $m$. The value of this reduced mass is $\mu = \frac{mM}{m+M}$, where, $m$=mass of the electron and $M$=mass of the nucleus. Thus, the Bohr eqn. (1.13) for the radius of a stationary orbit becomes

$$r_n = \frac{n^2 h^2}{4\pi^2 Z e^2 \mu}$$

(ii) *Introduction of the idea of elliptical orbits.* The existence of fine structure of the line spectrum implies that for each principal quantum number $n$, there are several energy levels close to each other instead of a single level only. Naturally, this requires the existence of a new quantum number which cannot be obtained from the Bohr model, for a circle has only one degree of freedom in the form of its radius or the angle of revolution at the centre. In order to overcome this difficulty, Sommerfeld proposed that in addition to the circular orbits of Bohr, the electron might also move in elliptical orbits around the nucleus, with the nucleus positioned at one of the two foci of the elliptical orbit. The ellipse possesses two degrees of freedom in the form of the semi-major axis ($n$) and the semi-minor axis ($k$). The ratio of these two axes $\left(\frac{n}{k}\right)$ is a measure of the eccentricity of the ellipse,

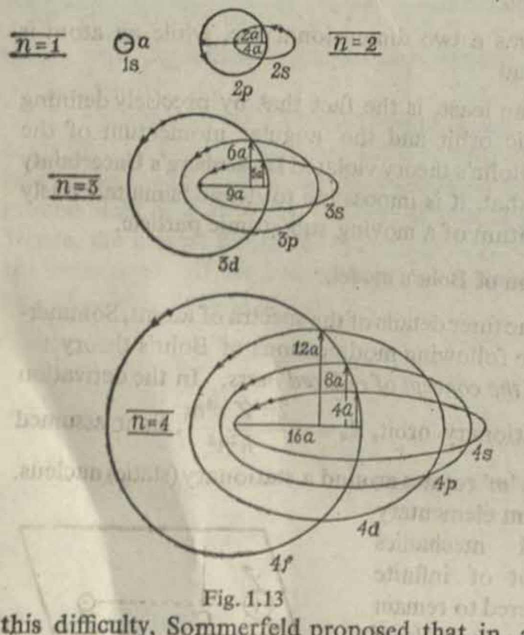

Fig. 1.13

the circle being a special case of ellipse whose semi-major axis is equal to the semi-minor axis ($n=k$). It can be shown by calculation that, for the angular momentum of the electron revolving in an elliptical orbit to be quantized, $k$ must assume only integral values ranging from 1, 2, 3 . . . . $n$ (figure 1.13 shows ellipses of different eccentricities). Since the value of $k=0$ implies that the electron goes through the nucleus (because when $k=0$, the ellipse becomes a straight line passing through the nucleus), it is excluded. Hence, for a particular value of $n$ above zero, there are more than one possible elliptical paths. Thus, for $n=2$, $k=1$ and 2 ; for $n=3$, $k=1,2$ and 3 and for $n=4$, $k=1,2,3$ and 4. For brevity and better accuracy, $k$ should be replaced by the quantum number $l$ which actually arises out of wave mechanical model (see later). This new quantum number $l$, known as the azimuthal quantum number, is defined as $l=(k-1)$ and the angular momentum of the electron in such an elliptical orbit is

$$mvr=\sqrt{l(l+1)}\,\frac{h}{2\pi}.$$

Just like the $\frac{n}{k}$ ratio, $l$ determines the shape of the orbit and for each value of the principal quantum number, $n$, there can be $n$ different orbits or energy sublevels corresponding the possible values of $l$, starting from zero upto $(n-1)$. In Bohr's original theory, it was assumed that all orbits with the same $n$-value would be *degenerate*, *i.e.* of equal energy. This idea failed to explain the existence of fine structure lines of the hydrogen spectrum which required additional electron jump within an energy-level designated by a particular value of the principal quantum number, $n$. Sommerfeld's idea of elliptical orbits provided the possiblity of additional electron jumps between the different orbits designated by different values of the azimuthal quantum number, $l$, corresponding to a particular value of $n$. The possible values of $l$, corresponding to particular $n$-values are given in the Table 1.1.

TABLE 1.1

| Principal quantum number, $n$ | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Azimuthal quantum number, $l$ [$l$ having all values from 0 to $(n-1)$] | 0 | 0,1 | 0,1,2 | 0,1,2,3 |

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Again, such different orbits are denoted by some letters of the alphabet. An orbit with $n=1$ and $l=(1-1)=0$ is designated as the 1*s* orbit. An orbit with $n=2$ and $l=1$ is known as the 2p orbit and an orbit with $n=3$ and $l=2$ is denoted as the 3d orbit. The different orbits, designated by different *l* values and the corresponding letter symbols are presented in table 1.2.

TABLE 1.2

| Different values of the azimuthal quantum number, *l* | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Letter symbol | *s* | *p* | *d* | *f* | *g* |

The number of different orbits designated by *n*-values of 1 – 4 and the corresponding *l*-values, along with their letter symbols are given in table 1.3.

TABLE 1.3

| Principal quantum number, *n* | Azimuthal quantum number, *l* | Letter symbol* |
|---|---|---|
| 1 | 0 | 1*s* |
| 2 | 0 | 2*s* |
| | 1 | 2*p* |
| 3 | 0 | 3*s* |
| | 1 | 3*p* |
| | 2 | 3*d* |
| 4 | 0 | 4*s* |
| | 1 | 4*p* |
| | 2 | 4*d* |
| | 3 | 4*f* |

The shapes of the different orbits corresponding to the different *n*- and *l*-values given in Table 1.3 are represented in Fig. 1.13. However, this modification not being adequate to fully account for the fine structure lines in the spectra, Sommerfeld introduced relativistic correction and bettered his model significantly.

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*Note that the number preceeding the letter symbol denotes the corresponding n-value, *i.e.*, the energy-shell in which that particular orbit exists.

The well-known relativity equation, expressing the relation between the rest mass and the mass of a moving particle, is

$$m=\frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}} \quad \ldots \quad \ldots \quad \ldots \quad (1.21)$$

where, $m_0$ =rest mass of the particle, $m$ =mass of the moving particle, $v$=velocity of the moving particle, c=velocity of light. This equation is applicable to the electron and implies that the mass of the moving particle increases with the increase of its velocity. We also know from Kepler's law that the velocity of a body moving in an elliptical orbit is maximum when it is nearest to the focus of the ellipse (perihelion) and is minimum when it is furthest from the focus (aphelion). Hence, the mass of an electron moving in an elliptical orbit becomes greatest at the perihelion and least at the aphelion positions. Due to its increased mass at the perihelion position, the electron is pulled with a greater force towards the nucleus. This effect compels the electron to deviate from its orginal orbit to a new and identical elliptical path which lie in the same plane, the perihelion position moving each time the electron completes a revolution. As a result, the entire electron-orbit moves or *precesses* (*Sommerfeld's precession*) round the nucleus as shown in Fig. 1.14.

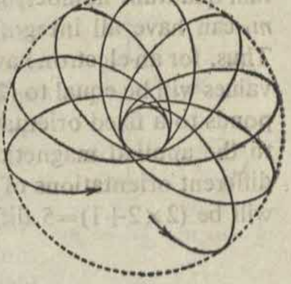

Fig. 1.14

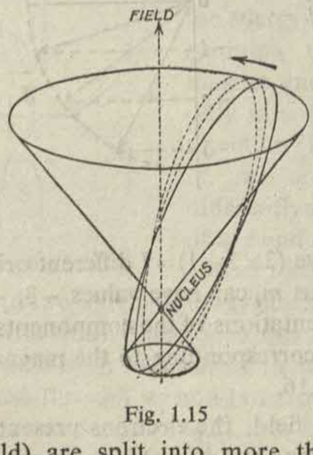

Fig. 1.15

This precessional movement of the orbit will result in small energy differences depending on the position of the orbit, and it is reflected in the fine structure of the atomic spectra.

When the radiating atom (the source of radiation) is placed in a magnetic field) some spectral lines (which are to appear as single lines in absence of the magnetic field) are split into more than one component lines. This phenomenon is known as the *Zeeman Effect*.

In order to explain such splitting of some spectral lines when the radiating atom is put in a magnetic field, a new quantum number became necessary. When placed in a magnetic field, the angular momentum vector undergoes a precessional movement around the direction of the magnetic field and describes a cone with the magnetic vector as the axis (Fig. 1.15). This phenomenon is known as *Larmor precession.*

The observed magnetism is determined by the value of the magnetic quantum number, $m_l$. Since this magnetism originates from the angular momentum of the electron, it is quite logical that the values of $m_l$ will depend on the value of the orbital angular momentum quantum number, $l$. Theory predicts and experiments show that, $m_l$ can have all integral values between $-l$ and $+l$, including zero. Thus, for an electron having a particular value of $l$, the number of $m_l$ values will be equal to $(2l+1)$, zero included. Each value of $m_l$ corresponds to a fixed orientation of the angular momentum vector relative to the applied magnetic field. For $l=1$, there will be $(2\times1+1)=3$ different orientations of the orbit in a magnetic field. For $l=2$, there will be $(2\times2+1)=5$ different orientations of the orbit under similar

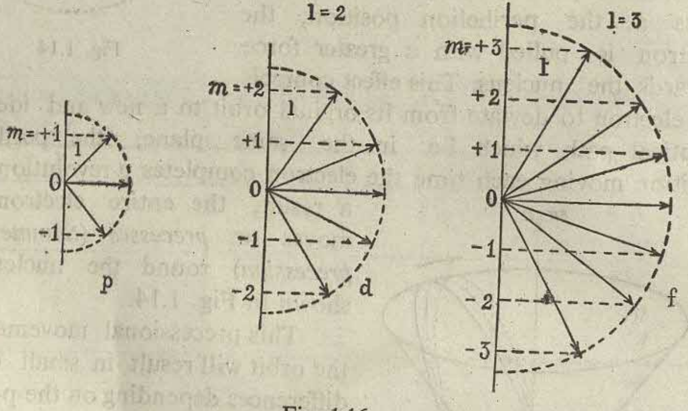

Fig. 1.16

conditions. Similarly, for $l=3$, we have $(2\times3+1)=7$ different orientations of the orbit in a magnetic field as $m_l$ can have values $-3$, $-2$, $-1$, $0$, $+1$, $+2$ and $+3$. All these orientations of the components of $l$ for each value of $n$ (*i.e.* the values corresponding to the magnetic quantum numbers) are shown in Fig 1.16.

Thus, when placed in a magnetic field, the electrons present in a particular energy sub-level (excepting the $s$ sub-levels) take up certain specific orientations in space around the atomic nucleus. *Such regions in space are known as orbitals and they represent well-defined regions* *in space where the probability of finding an electron of a particular energy is very high.*

Now we see that every given combination of $n$ and $l$ represents a number of identical orbits which are inclined in different directions in space with respect to a reference direction, such as the direction of an imposed magnetic field. The nature of inclination of each such orbit with the reference direction is regulated by the magnitude and sign of the corresponding magnetic quantum number $m_l$. Positive sign of $m_l$ denotes the components of $l$ in the reference direction (*i.e.* in the direction of the imposed magnetic field) and the negative sign denotes components opposite to the direction of the field.

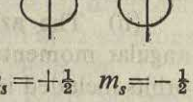

Fig. 1.17

At this stage the spectrocopists found that these three quantum numbers $n$, $l$, and $m_l$ are not sufficient to fully account for the fine structure of spectral lines. It was observed that the lines in the spectra of the alkali metals are not the single lines arising out of every combination of $n$, $l$ and $m_l$, as predicted by the Bohr-Sommerfeld theory. Such single spectral lines (singlets) were found to consist of two closely spaced lines (*doublets*). Uhlenbeck and Goudsmit in 1925 proposed that, such doublets originate from the existence of different energy states resulting from electrons spinning in opposite directions about an axis. Hence, a fourth quantum number, the spin quantum number, designated by $m_s$, is essential to completely define the energy-state of an electron. A charged particle spinning about its own axis behaves as a tiny magnet and an electron can spin about its axis only in a (i) *clockwise* or an (ii) *anticlockwise* direction (Fig. 1.17.) and hence, only two values of $m_s$ are possible. The energies of such differently spinning electrons (having same values of $n$, $l$ and $m_l$), when placed in a magnetic (or electric) field, should be different and would give rise to two different energy-states reflected in the doublet nature of some spectral lines. Validity of this idea was demonstrated by the famous Stern-Gerlach experiment in which a beam of hydrogen atoms, was passed through an non-homogeneous magnetic field and the atomic beam was found to split into two (Fig. 1.18).

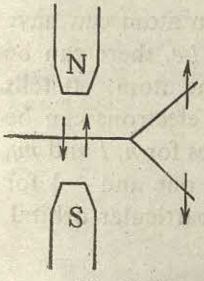

Fig. 1.18

Such a splitting of the atomic beam in a magnetic field proves that the electrons in the atoms were behaving as tiny magnets spinning in opposite directions. Thus, there could be no doubt about the fact that in addition to its orbital angular momentum, an electron also possesses spin-angular momentum. Like the orbital angular momentum, spin-angular momentum is also quantized and may have a value of either $+\frac{h}{2\pi}$ or $-\frac{h}{2\pi}$. These values, designated as spin quantum numbers, are generally written as $m_s=+\frac{1}{2}$ or $-\frac{1}{2}$.

**Significance of quantum numbers :**

Thus, we find that in order to fully define the energy-state of of an electron, four quantum numbers, $n$, $l$, $m_l$ and $m_s$ are essential. The physical significance of each of these four quantum numbers may be interpreted in the following way :

(i) The principal quantum number ($n$) determines the energy of the electron. It defines the electron-shell.

(ii) The azimuthal quantum number ($l$) determines the orbital angular momentum and thereby describes the shape of the electron-orbits included in the energy-shell denoted by $n$.

(iii) The magnetic quantum number ($m_l$) determines the position (orientation) of the electron-orbit in space.

(iv) The spin quantum number ($m_s$) determines the direction of spin of the electron with a particular set of values of $n$, $l$ and $m_l$.

## PAULI'S EXCLUSION PRINCIPLE.

This principle states that, no two electrons in an atom can have the same values for all the four quantum numbers, *i.e.* there can be only one electron in each possible energy-state in the atom. It tells us that, in a particular orbital, a maximum of two electrons can be allowed. The two electrons will have the same values for $n$, $l$ and $m_l$, but their spin quantum numbers will be $+\frac{1}{2}$ for the one and $-\frac{1}{2}$ for the other. Such pairs of electrons, residing in any particular orbital, are said to be "spin-paired".

## ELECTRONIC CONFIGURATION OF ATOMS.

Most of the important properties of the atoms are dependent on the number of electrons they possess and especially on the way they are arranged among the different orbitals differing in energy. In order to know how this happens, the knowledge of the electronic configurations of the atoms of different elements is essential. With the concept of the four quantum numbers and the **Pauli's Exclusion Principle** at our disposal, the proces of gradual build-up of the electronic structure of the different atoms can now be elucidated.

When $n=1$, $l$ can have only one value, $(1-1)=0$. Similarly, $m_l$ will also have one value, zero. The spin quantum number may have two values, $+\frac{1}{2}$ and $-\frac{1}{2}$. Thus, for electrons having the principal quantum number, $n=1$, only two sets of values for the four quantum numbers are possible (Table 1.4).

TABLE 1.4

| $n$ | $l$ | $m_l$ | $m_s$ | Orbital |
|---|---|---|---|---|
| 1 | 0 | 0 | $+\frac{1}{2}$ | 1*s* |
| 1 | 0 | 0 | $-\frac{1}{2}$ | |

Since the exclusion principle must be operative, it follows that only two electrons having identical values of $n$, $l$ and $m_l$, but differing in spin quantum number '$m_s$', can be present in the energy-level designated by principal quantum number, $n=1$, and both of them are *s* electrons. Thus, the *s*-orbital can accomodate a maximum of 2 electrons.

For an energy-shell characterised by $n=2$ (the L-shell), the maximum number of electrons characterised by the different possible values of $n$, $l$, $m_l$ and $m_s$, and following the exclusion principle, is equal to eight. Of these 8 electrons, 2 are *s* electrons and 6 are *p* electrons as is shown in Table 1.5. In a similar manner, it can be shown that the *d*-orbital can contain a maximum of 10 and *f*-orbital a maximum of 14 electrons. All these details are given in Table 1.5.

It may be observed here that the total number of electrons in any one energy-shell, designated by a particular value of $n$, is given by the expression $2n^2$. For the K-shell, $n=1$,

$$\therefore\quad 2n^2=2\times1^2=2.$$

For $n=2$, $2n^2=2\times2^2=8$ (L-shell).

for $n=3$, $2n^2=2\times3^2=18$ (M-shell).

for $n=4$, $2n^2=2\times4^2=32$ (N-shell).

**Energy order of orbitals and electronic configuration of the atoms of the elements.**

It may be noted also that the maximum number of electrons in a particular energy-shell can also be obtained by applying Pauli's exclusion principle.

Since the application of quantum mechanics to multi-electron systems is difficult, **the simplest procedures used for the approximate description of multi-electron atoms are the extensions of those principles used to describe the hydrogen atom.** The atomic orbitals of such atoms are taken to be similar to those of the hydrogen atom, each orbital being defined by a set of four quantum numbers which are the same as those of the hydrogen atom. For writing the electronic

TABLE 1.5. Arrangement of electrons in different quantum levels.

| Shell | n | l | $m_l$ | s | No. of electrons for each set of n, l and $m_l$ | | Electronic configurations | Total no. of electrons $2n^2$. |
|---|---|---|---|---|---|---|---|---|
| K | 1 | 0 | 0 | $\pm\frac{1}{2}$ | 2 | | $1s^2$ | 2 |
| L | 2 | 0 | 0 | $\pm\frac{1}{2}$ | 2 | | $2s^2$ | 8 |
| | | 1 | −1 | $\pm\frac{1}{2}$ | 2 | 6 | $2p^6$ | |
| | | | 0 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +1 | $\pm\frac{1}{2}$ | 2 | | | |
| M | 3 | 0 | 0 | $\pm\frac{1}{2}$ | 2 | | $3s^2$ | 18 |
| | | 1 | −1 | $\pm\frac{1}{2}$ | 2 | 6 | $3p^6$ | |
| | | | 0 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +1 | $\pm\frac{1}{2}$ | 2 | | | |
| | | 2 | −2 | $\pm\frac{1}{2}$ | 2 | 10 | $3d^{10}$ | |
| | | | −1 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | 0 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +1 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +2 | $\pm\frac{1}{2}$ | 2 | | | |
| N | 4 | 0 | 0 | $\pm\frac{1}{2}$ | 2 | | $4s^2$ | 32 |
| | | 1 | −1 | $\pm\frac{1}{2}$ | 2 | 6 | $4p^6$ | |
| | | | 0 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +1 | $\pm\frac{1}{2}$ | 2 | | | |
| | | 2 | −2 | $\pm\frac{1}{2}$ | 2 | 10 | $4d^{10}$ | |
| | | | −1 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | 0 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +1 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +2 | $\pm\frac{1}{2}$ | 2 | | | |
| | | 3 | −3 | $\pm\frac{1}{2}$ | 2 | 14 | $4f^{14}$ | |
| | | | −2 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | −1 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | 0 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +1 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +2 | $\pm\frac{1}{2}$ | 2 | | | |
| | | | +3 | $\pm\frac{1}{2}$ | 2 | | | |

configuration of an atom in the **ground state,** it is assumed that the atom starts with a positive nucleus surrounded by empty orbitals.

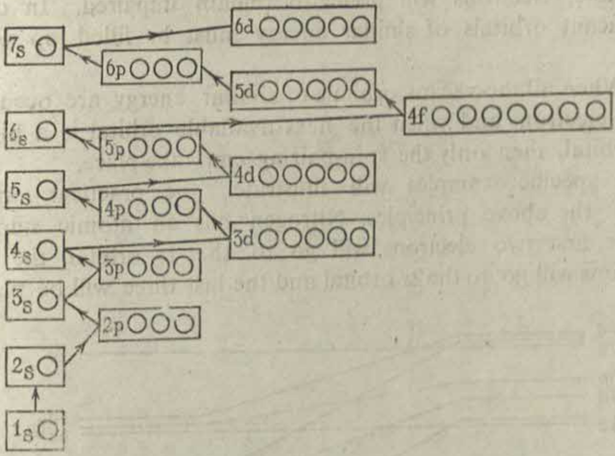

Fig. 1.19

The electrons are gradually fed into the orbitals, one by one, in the order of increasing energy, till the nuclear charge is balanced by the total electronic charge. This gradual build-up of the electronic configuration of the atoms is known as the **Aufbau Principle,** and is based on the following rules :

1. The lowest energy orbital is filled up first and then only elecrons pass on to the next higher energy orbital. The relative positions of the different electronic orbitals as obtained from spectroscopic studies are shown in Fig. 1.19, where the energy of the orbitals increases upwards.

Several other types of diagrams to reflect the order of the gradual filling up of the electronic orbitals were proposed. One such useful scheme is shown in Fig. 1.20, in which the orbitals are occupied in the order they are struck by the series of parallel diagonal arrows.

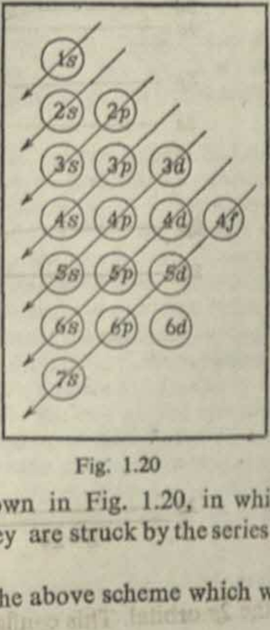

Fig. 1.20

There are a number of exceptions to the above scheme which will be enumerated later.

2. **Hund's Rule of Maximum Multiplicity.**

As long as vacant orbitals of similar energy (degenerate orbitals) are available, electrons will prefer to remain unpaired. In other words, vacant orbitals of similar energy must be filled up singly at first.

3. When all the vacant orbitals of similar energy are occupied by single electrons and when the next available orbital is a higher energy orbital, then only the spin-pairing can take place.

Some specific examples will illustrate the practical application of the above principles. Nitrogen has an atomic number 7; so, the first two electrons will go to the 1*s* orbital, the next two electrons will go to the 2*s* orbital and the last three will be placed in the 2*p* orbital. This configuration is written as $1s^2 2s^2 2p^3$. In a similar

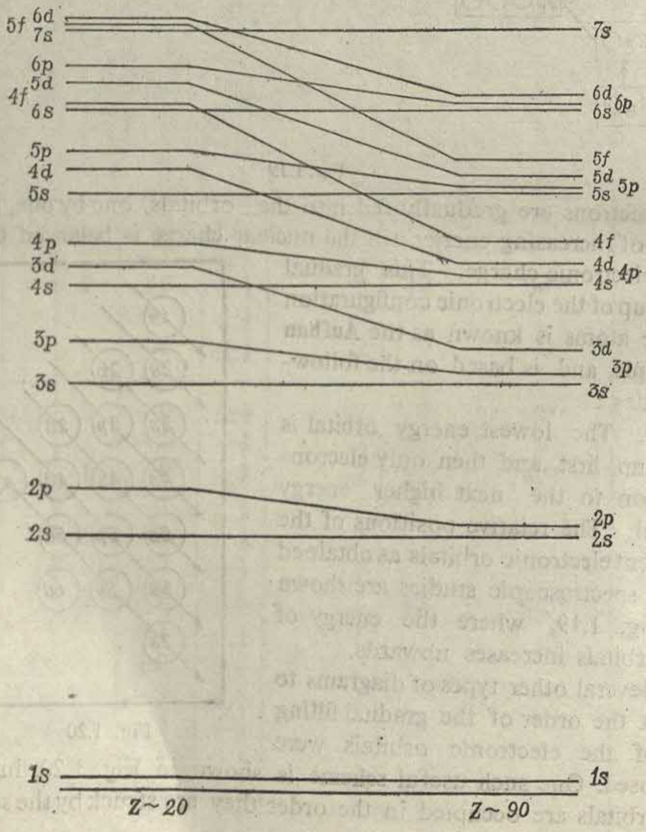

Fig. 1.21

manner, the electronic configuration of oxygen (at. no. 8) is $1s^22s^22p^4$ and that of fluorine (at. no.9) is $2s^22s^22p^5$ and so on. The eleotronic configurations of the elements from hydrogen to argon are given in Table. 1.6. Each box ☐ represents an orbital and an arrow ( ↑ ) stands for a single unpaired electron and a double arrow, pointing in opposite directions ( ⇅ ), represents a spin-paired electron-pair.

It can be seen from fig 1.21 that as atomic number increases, the relative energies of all the levels do not change to the same extent. Of the different levels *s*, *p*, *d* and *f*, the *s* levels are not influenced effectively and though the *p* levels are influenced slightly by the change in atomic number, they retain their relative positions. But, the *d* and *f* levels are influenced to a very large extent. Thus, in the atoms with $Z<20$, the 3*d*-orbital lies above 4s. But, for atoms with $Z\geq21$, this order is reversed, and electrons are allowed to occupy the 3d-levels from scandium (Z=21) instead of entering the 4p-level. This is the reason of the appearence of the first transition series with scandium (Z=21) as the starting element. For identical reasons, the second transition series appears at Z=39 (Y) and the third transition series begins from Z=58 (Lu).

### (n+*l*) Rules and their applicability.

Even if the details of the energy-level data are not known, the order in which the orbitals are occupied can be anticipated quite correctly. This may be done by the application of the so-called (n+*l*) rules (which are purely empirical in character) which may be stated as follows :

(i) Of the two possible closely spaced energy-levels, an added electron will always perfer the level with the lower (n+*l*) value.

(ii) If two such competing energy-levels have the same (n+*l*)-value, then the in-coming electron will enter the level with lower n-value. The applicability of these two rules can be verified by considering the cases of potassium (Z=19) and scandium (Z=21).

The case of argon (Z=18) is quite straight-forward, the last electron (the 18th electron) entering an already singly occupied 3p-level.For the next element potassium (Z=19), the last electron (the 19th electron) may enter either the 3d- or the 4s-level. For the 3d-level, n=3 and *l*=2, which gives (n+*l*)=(3+2) =5. For the 4s level, n=4 and *l*=0, giving (n+*l*)=(4+0)=4. Hence, the last electron in potassium is placed into the 4s-level and the electronic configuration of potassium is $1s^22s^22p^6$ $3s^23p^64s^1$. In the next element calcium (Z=20) the last electron (the 20th electron) enters the 4s-level for the same reason and calcium possesses the electronic configuration $1s^22s^22p^63s^23p^64s^2$. However, in the case of scandium (Z=21), the last electron may enter either 4p or the 3d level. For 4p, n=4 and *l*=1, giving (n+*l*)=(4+1)=5. For 3d, n=3 and d=2 and hence, (n+*l*)=(3+2)=5. So, here we find two cases with identical (n+*l*) value. According to the second (n+*l*) rule, the last electron should enter the level with lower n-value, *i.e.* it should enter the 3d-level in preference to the 4p-level and this is found to be the actual case. Hence, these two (n+*l*) rules are sometimes very useful in predicting the relative order of filling up of the electron-levels.

We find that, with the increase in atomic number of the elements, representation of the electronic configurations become more and

TABLE 1.6

### ELECTRONIC CONFIGURATIONS OF ELEMENTS FROM HYDROGEN TO ARGON

| ELEMENTS | ATOMIC NUMBER | ELECTRONIC CONFIGURATION | $1s$ | $2s$ | $2p$ | $3s$ | $3p$ |
|---|---|---|---|---|---|---|---|
| H | 1 | $1s^1$ | [↑] | | | | |
| He | 2 | $1s^2$ | [↑↓] | | | | |
| Li | 3 | $1s^2 2s^1$ | [↑↓] | [↑] | | | |
| Be | 4 | $1s^2 2s^2$ | [↑↓] | [↑↓] | | | |
| B | 5 | $1s^2 2s^2 2p^1$ | [↑↓] | [↑↓] | [↑][ ][ ] | | |
| C | 6 | $1s^2 2s^2 2p^2$ | [↑↓] | [↑↓] | [↑][↑][ ] | | |
| N | 7 | $1s^2 2s^2 2p^3$ | [↑↓] | [↑↓] | [↑][↑][↑] | | |
| O | 8 | $1s^2 2s^2 2p^4$ | [↑↓] | [↑↓] | [↑↓][↑][↑] | | |
| F | 9 | $1s^2 2s^2 2p^5$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑] | | |
| Ne | 10 | $1s^2 2s^2 2p^6$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | | |
| Na | 11 | $1s^2 2s^2 2p^6 3s^1$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | [↑] | |
| Mg | 12 | $1s^2 2s^2 2p^6 3s^2$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | [↑↓] | |
| Al | 13 | $1s^2 2s^2 2p^6 3s^2 3p^1$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | [↑↓] | [↑][ ][ ] |
| Si | 14 | $1s^2 2s^2 2p^6 3s^2 3p^2$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | [↑↓] | [↑][↑][ ] |
| P | 15 | $1s^2 2s^2 2p^6 3s^2 3p^3$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | [↑↓] | [↑][↑][↑] |
| S | 16 | $1s^2 2s^2 2p^6 3s^2 3p^4$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | [↑↓] | [↑↓][↑][↑] |
| Cl | 17 | $1s^2 2s^2 2p^6 3s^2 3p^5$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | [↑↓] | [↑↓][↑↓][↑] |
| Ar | 18 | $1s^2 2s^2 2p^6 3s^2 3p^6$ | [↑↓] | [↑↓] | [↑↓][↑↓][↑↓] | [↑↓] | [↑↓][↑↓][↑↓] |

more cumbrous and space-consuming. So, in writing the electronic configurations of the many-electron atoms, it is often convenient to omit the assignment of the inner electrons constituting the preceding inert gas atom and write the configuration of only those electrons which are outside that inert gas structure. Thus, in writing the electronic configurations of the so-called **first row transition elements** from scandium (at. no. 21) to zinc (at. no. 30), the electronic arrangement of the first 18 electrons (corresponding to the structure of the argon atom) is represented as $\boxed{\text{Ar}}$ in Table 1.7.

TABLE 1.7.

| ELEMENTS | ATOMIC NUMBER | ELECTRONIC CONFIGURATION | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 4s | 3d | | | | |
| Scandium | 21 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ | Ar | ↑↓ | ↑ | | | | |
| Titanium | 22 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ | Ar | ↑↓ | ↑ | ↑ | | | |
| Vanadium | 23 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ | Ar | ↑↓ | ↑ | ↑ | ↑ | | |
| Chromium | 24 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ | Ar | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ |
| Manganese | 25 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$ | Ar | ↑↓ | ↑ | ↑ | ↑ | ↑ | ↑ |
| Iron | 26 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ | Ar | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | ↑ |
| Cobalt | 27 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ | Ar | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ | ↑ |
| Nickel | 28 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ | Ar | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ |
| Copper | 29 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ | Ar | ↑ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ |
| Zinc | 30 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ | Ar | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ |

According to the Aufbau principle discussed before, chromium (at. no. 24) and copper (at. no. 29) should have the following electronic configurations (see fig. no. 1.22).

But, in the above table, the electronic configurations are shown as different. The reason behind is the **extra stability of the half-filled and**

**the full-filled *d*-orbitals** when compared to the alternative arrangements. Details of electronic configuration of the other elements, along with

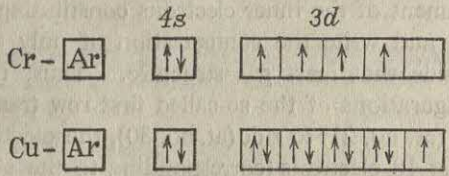

Fig. 1.22.

the properties associated with the type of electronic configuration, will be discussed later.

**Violation of the Aufbau principle.**

The actual electronic configuration of the atoms of quite a few elements are found to differ slightly from the configuration predicted by the Aufbau principle. Such deviations generally involve the placement of one or two n*s*-electrons before electrons are fed into an inner (n – 1)*d*-level. The relevant outermost electronic configurations of some of the atoms which deviate from regularity are given below :

TABLE 1.8

| Name of the element | Atomic number | Electron-arrangement predicted by the Aufbau principle | Actual arrange-ment |
|---|---|---|---|
| Chromium (Cr) | 24 | $3d^4 4s^2$ | $3d^5 4s^1$ |
| Copper (Cu) | 29 | $3d^9 4s^2$ | $3d^{10} 4s^1$ |
| Molybdenum (Mo) | 42 | $4d^4 5s^2$ | $4d^5 5s^1$ |
| Palladium (Pd) | 46 | $4d^8 5s^2$ | $4d^{10} 5s^0$ |
| Silver (Ag) | 47 | $4d^9 4s^2$ | $4d^{10} 5s^1$ |
| Platinum (Pt) | 78 | $5d^8 6s^2$ | $5d^9 6s^1$ |
| Gold (Au) | 79 | $5d^9 6s^2$ | $5d^{10} 6s^1$ |

Such deviation occur because the energy-difference between n*s* and (n – 1)*d* level is rather small. Extra stability of half-filled and full-filled orbitals also contribute to some extent.

**Shortcomings of the classical atomic model.**

The Bohr-Sommerfeld atomic model (which has already been discussed) is mainly empirical in nature and took shape out of the attempts to explain the characteristic features of atomic spectra, and the four quantum numbers $n$, $l$, $m_l$ and $m_s$ were introduced *ad hoc* solely for this purpose. It lacked a sound theoretical basis and though it incorporated in it the quantum theory of radiation and utilised relativistic approach to some extent, it is regarded as the classical atomic model. The major shortcomings of this classical atomic model may be outlined as follows :

1. It failed to explain fully the spectral characteristics of systems containing more than one electron.
2. It considered the electron solely as a particle.
3. It violated Heisenberg's **Uncertainty Principle** (see later) by making an attempt to simultaneously define the position and the velocity of the moving electron.
4. It failed to explain the directional character of chemical bonding.*

Such failures necessarily required new atomic model having a sound theoretical basis and capable of overcoming the defects of the classical model. Such an atomic model is the **wave mechanical model of the atom.** The experimental and theoretical developments which led to the formulation of the wave mechanical atom will now be discussed briefly.

**Dual nature of light.**

In the past, light has been considered either as particles or as waves. Newton considered light as particle in his famous *corpuscular theory of light*. But, Huygens' recognition of the wave character of light in his famous *wave theory*, received widest recognition when it successfully explained the interference and the diffraction phenomena.

The wave theory of light held the stage for quite a long time until the revival of the corpuscular theory, which only could satisfactorily explain the photo-electric effect.

**Photo-electric effect.**

When light of appropriate wavelength (or frequency) is allowed to fall on some metals (e.g. the alkali metals, the alkaline earth metals, zinc *etc.*), the metals give off electrons. Such a phenomenon of emission of electrons from metal surfaces by the effect of light radiation is known as the *photo-electric effect*. For example, light in the visible region can emit electrons from the alkali metals like rubidium and cesium. But, to induce photo-electric effect in zinc and other metals, light of the ultraviolet region is necessary.

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*A large variety of geometrical shapes observed in the cases of different molecules and polyatomic ions clearly indicate that the electrons responsible for chemical bonding must be localised along bond directions. But, according to the classical model, the electrons are constantly moving round the nucleus and hence cannot be localised in any preferred direction. So, it fails to explain the directional nature of chemical bonding.

The following characteristic features of the photo-electric effect are recognised :

(i) **For each metal, there is a critical wavelength, and light of higher wavelength cannot emit photo-electrons.** This wavelength is known as the **Photo-electric threshhold.**

(ii) The kinetic energy of such photo-electrons is inversely proportional to the wavelength of the incident light $\left(\text{K.E} \propto \frac{1}{\lambda}\right)$, but,

(iii) it does not depend on the intensity of the radiation.

(iv) However, the rate of emission of photo-electrons is directly proportional to the intensity of incident radiation.

In 1905, these observations were interpreted by Einstein by invoking the idea of light-quantum or photon which is nothing but the recognition of the particle-nature of light. According to Einstein's theory of photo-electric effect, radiation incident on the metal plate may be regarded as packets of radiation or photons with energy h$\nu$. When such a photon falls on a metal plate, one part of the energy of this photon is used up to make the electorn escape from the metal (which is the ionization energy of the metal, $E_I$) and the remaining portion of the energy of the photon is given up to the photo-electron as its kinetic energy. Einstein's famous photo-electric equation is

$$h\nu = E_I + \tfrac{1}{2}mv^2 \qquad \ldots. \ (1.22)$$

This equation explains why the energy of the photo-electrons is related to the frequency or wavelength of the incident radiation, and it is the recognition of corpuscular (or particulate) nature of radiation which enabled Einstein to explain the photo-electric effect. Explanation of the scattering of X-rays with electrons—Compton-effect—established the particle character of radiation. Hence, at the beginning of the 20th century the dual nature of radiation was well-established.

**Dual nature of matter.**

As pointed out before, the electron is exclusively regarded as a negatively charged particle. The wave character of the electron was recognized for the first time by the French physicist Louis de Broglie in 1924 while making a theoretical study of the quantum theory. He recognised a striking analogy between the properties of the photons or light quanta and the moving electron. He arrived at his idea from purely mathematical consideration in the following manner :

The energy (E) of a photon of frequency $\nu$ is given by $E=h\nu$.
Again, the mass of a photon (m) is related to its energy by the Einstein equation, $E=mc^2$. So, we can write $E=h\nu=mc^2$ ...(1.23)
(c=velocity of light)

Momentum is a property directly and inseparably associated with the particle nature, and the momentum of the light photon of mass $m$ and velocity $c$ is $mc$. Now, we can arrive at the momentum expression for the light photon by dividing both sides of the eqn. $mc^2=h\nu$ by $c$. Thus we get $mc=h\times\frac{\nu}{c}$ .. .. (1.24)

Putting $\frac{\nu}{c}=\frac{1}{\lambda}$ in the above eqn., we get,

$$mc=\frac{h}{\lambda} \quad .. \quad .. \quad (1.25)$$

$$\text{or, } \lambda=\frac{h}{mc} \quad .. \quad .. \quad (1.26)$$

This equation expresses the relation between the wave nature of the photon designated by $\lambda$ (wave length) and its particle nature designated by its momentum $mc$. De Broglie pointed out that eqn. (1.26) could be applied to an electron by putting the mass of the electron $m_e$ in place of $m$ (the mass of the photon) and replacing the velocity of the photon '$c$' by the velocity '$v$' of the electron. Thus, in the case of the electron, the eqn. (1.26) takes the form, $\lambda = \frac{h}{m_e v} = \frac{h}{p}$ .. (1.27) where $p$ is the momentum of the electron. In fact, this equation holds good for any particle of mass $m$ and a known velocity and this equation is the mathematical expression for the wave-particle duality of matter. The wavelengths of some particles, calculated by using de Broglie eqn. (1.27), are given in Table 1.9.

TABLE 1.9

| Particle | Mass (gm.) | Velocity cm/sec. | De Broglie wavelength (Å) |
|---|---|---|---|
| Electron | $9{\cdot}1 \times 10^{-28}$ | $1{\cdot}2 \times 10^{7}$ | 61 |
| Alpha particle | $6{\cdot}6 \times 10^{-24}$ | $1{\cdot}4 \times 10^{8}$ | 0·71 |
| Golf ball | 50 | $5 \times 10^{3}$ | $2{\cdot}65 \times 10^{-24}$ |
| Tennis ball | 100 | $2{\cdot}5 \times 10^{3}$ | $2{\cdot}65 \times 10^{-24}$ |

From de Broglie's hypothesis, it is clear that matter may exhibit both wave and particle nature and this analysis extends to all matter ranging from the electrons to the planet and even bigger bodies. However, from the data presented in Table 1.9, the wavelength associated with massive particle like the golf ball or the tennis ball are so short that we cannot measure them. Thus the concept of wave-particle duality is of real importance only in the case of very small particles like the electron. Experimental verification of de Broglie's prediction was made in 1927 by Davisson and Germer who showed that a beam of electrons could be diffracted by crystals (a thin nickel crystal was used) just as light or X-rays. As the occurrence of the phenomenon of diffraction can be accounted for only in terms of waves, the electrons in such experiments definitely behave as waves. Later on, neutron diffraction experiments lent further support to the wave-particle duality concept.

**The uncertainty principle.**

Firm establishment of the wave-particle duality concept inevitably led to the question whether a *thing* can justifiably considered strictly as a *particle or a wave.* If one insists that a *thing* is a *particle*, then we should be able to determine quantitatively its fundamental properties like *momentum* or *position* which are inseparably associated with particles. Such measurements, though extremely simple with macroscopic bodies (*e.g.* the planets, a foot ball, a tennis ball *etc.*), would be extremely difficult, if not impossible, in the case of very small particle like the electron. It is so, because the electron is too small to be seen directly and hence it can be observed only indirectly by perturbing it with an outside agency like an electric or magnetic field or a light photon. But, exposure of the electron to any such force will at once change its position or velocity (and hence its momentum). Heisenberg expressed this situation by stating that, **the more accurately the position of a particle like the electron is defined, the less accurately is its velocity known** and *vice versa*. This is the famous **Uncertainty principle** of Heisenberg. If $\Delta x$ represents the uncertainty in defining the position, and the uncertainty in defining the velocity is expressed as $\Delta v$, the mathematical expression for the uncertainty principle takes the form,

$$\Delta x.\ \Delta v \geq \frac{h}{4\pi} \qquad \ldots \qquad \ldots (1.28)$$

where $h$ = Planck's constant $= 6{\cdot}624 \times 10^{-27}$ erg-sec. This equation implies that it is impossible to know simultaneously both the position and the velocity of a small particle like the electron accurately, which is an alternative statement of the uncertainty principle. The classical atomic model, which incorporates the concept of an electron moving in a definite orbit, where both its position and velocity (and hence, momentum) are exactly known, must be replaced, since it is no longer possible to accept a *deterministic* model as it is in contradiction to the fundamental scientific principle—the uncertainty principle. Therefore, the wave mechanical atom, expressing the position and velocity in terms of probability, is a logical and inevitable outcome of our recognition of the probability character of our observations of the microscopic world.

### The physical basis of wave mechanics.

De Broglie's hypothesis led to the realization that the mathematics of wave behaviour may be applicable to the behaviour of electrons in atoms. It is well known that a vibrating string generates waves. When a string, fixed at two ends, vibrates, many wave-patterns are generated, of which all are not stable. Some of them damp out quickly, but others exist for quite a long time, repeating themselves over and over again. These stable patterns are known as the **standing waves** and they are generated when the amplitude of vibration is zero at the point of attachment of the string (Fig. 1.23). The wavelengths of such standing waves are obtained from the

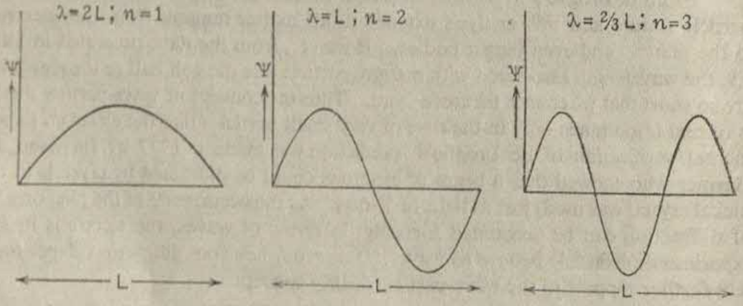

Fig. 1.23

general relation, $\lambda = \frac{2L}{n}$ .... (1.29) where $\lambda$=wavelength, L=distance between the points of attachment of the vibrating string, and $n$=1, 2, 3, 4 etc. The wavelengths of such standing waves take only certain values and those values are determined by the value of the integer $n$. Heisenberg and Schrodinger realised the significance of this observation and recognized that, unlike the classical atomic model (the Bohr-Sommerfeld model), in which the principal quantum number was introduced *ad hoc*, in the case of vibrating strings '*n*' automatically comes out of the physics of the situation. This realization led Schrodinger to make an attempt to describe the behaviour of the electrons in an atom in terms of the equations generally used for the vibrating strings. Thus, in the wave theory, an electron is conceived as a standing train of waves which extends around the nucleus in definite three dimensional patterns corresponding to the allowed values of $\lambda$ which signifiy only certain allowed values of the energy of the standing electron-waves.

For a particle like an electron moving in three dimensions in the field of the nucleus, the Schrodinger wave eqn. is

$$\frac{\delta^2\Psi}{\delta x^2}+\frac{\delta^2\Psi}{\delta y^2}+\frac{\delta^2\Psi}{\delta z^2}+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0 \quad .. \quad (1.30)$$

where $m$ =mass of the electron,

$V$ =potential energy of the electron,

$E$ =total energy of the electron,

$h$ =Planck's constant,

$\Psi$ =wave function or the eigenfunction of the electron representing the amplitude of the wave associated with the electron.

$x, y, z$ =coordinates of the electron.

The known quantities in this equation are $m$ (the mass of the electron) and V (potential energy of the electron), expressed as a function of the coordinates x,y, z. The solution of this second order differential equation gives the values of E (the quantised or allowed energies of the electron) and $\Psi$, or the **wave function.** In other words, the solution of this equation gives the electron-distribution in space as well as the permitted energy states of the electron. When this equation is applied to a system like the hydrogen atom, it is found that it can be solved only when E takes on *certain values* which are related by integers. Hence, the concept of quantized energy levels and quantum numbers are spontaneous consequences of the wave theory and need not be introduced *ad hoc* to explain the experimental facts, as is done in the Bohr theory.

**Significance of (i) $\Psi$ and (ii) $\Psi^2$** : (i) As already mentioned $\Psi$ denotes the amplitude of a three-dimensional stationary electron-wave.

(ii) According to the uncertainty principle, it is impossible to locate the electron in an atom (which is always moving) with precision. But, the nature of the wave-function $\Psi$ is such that square of the magnitude of $\Psi$, $/\Psi/^2$ represents the probability of finding the electron in a definite volume of space surrounding the nucleus. It is a mathematical expression of how the probability of finding an electron varies from place to place. The total probability of occurrence of a single electron in space extending to infinity must always be unity and this can be expressed as

$$\int_{-\infty}^{+\infty}\Psi^2 dv=1 \quad .. \quad .. \quad (1.31)$$

where d$v$ is an element of volume, dx.dy.dz. This is known as the condition of normalization and the corresponding wave function $\Psi$ is said to be normalised.

Because of the spherical symmetry of the atom, the wave functions are most suitably expressed in terms of spherical polar coordinate system with the nucleus as its origin.

When the position of the electron is expressed in terms of polar coordinates, the wave equation (1.30) assumes the form

$$\frac{1}{r^2}\frac{\delta}{\delta r}\left(r^2\frac{\delta\Psi}{\delta r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\delta^2\Psi}{\delta\phi^2}+\frac{1}{r^2\sin\theta}\frac{\delta}{\delta\theta}\left(\sin\theta\frac{\delta\Psi}{\delta\theta}\right)$$
$$+8\pi^2\mu\,(E-V)=0 \qquad \ldots\ldots(1.32)$$

Where, r,$\theta$ and $\phi$ are the polar coordinates of the electron with respect to the nucleus

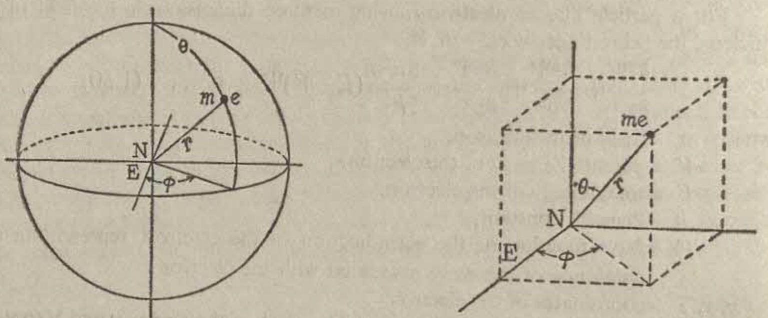

Fig. 1.24 (a) and (b)

N as origin. The situation is depicted in figure 1.24 [See Fig. 1.24(b) also for the relation between the Cartesian and the polar coordinates].

The boundary conditions that are to be imposed on $\Psi$ to obtain meaningful solutions of the eqn. (1.32) are : $\Psi$ and its first derivative are (i) continuous, (ii) single-valued and (iii) finite. Solutions of the wave equation satisfying these conditions are known as *eigenfunctions.*

It can be shown mathematically that each allowed solution of the wave eqn. **(1.32) i. e. wave function** $\Psi\,(r,\theta,\phi)$ can be expressed as

$$\Psi\,(r,\theta\ \phi)=R(r).\Theta(\theta).\Phi\ \phi \qquad \ldots(1.33)$$

where, R (r) is a function dependent on the distance r from the nucleus, which depends on the quantum numbers n and l — the principal and the azimuthal quantum numbers. This is why R (r) is also written as R $(r)_{n,l}$ or $R_{n,l}\,(r)$.

$\Theta(\theta)$ is a function which depends on $\theta$, which again depends on the azimuthal quantum number l and the magnetic quantum number $m_l$. Hence, $\Theta(\theta)$ is also written as $\Theta(\theta)_{l,m_l}$ or $\Theta_{l,m_l}(\theta)$.

$\Phi(\phi)$ is a function of $\phi$ which, in its turn depends only on the magnetic quantum number $m_l$. Thus, $\Phi(\phi)$ is also represented as $\Phi(\phi)m_l$ or $\Phi m_l(\phi)$. Hence, eqn. (1.33) may now be presented as $\Psi(r,\theta,\phi)_{n,l,m_l}=R(r)_{n,l}\cdot\ \Theta(\theta)_{l,m_l}\ \ \Phi(\phi)$ . . . (1.34) Both the second and the third terms in eqn. (1.34), which represent the different angular parts of the wave functions, may be combined together as Y $(\theta,\phi)l,m_l$ denoting the total angular wave function.

Thus, eqn. (1.34) may be rewritten as $\Psi(r,\theta,\phi)_{n,l,m_l}.=R(\mathrm{r})_{n,l}.Y(\theta,\phi)_{l,m_l}$ . . .(1.35) This total wave function $\Theta(\mathrm{r},\theta,\phi)_{n,l,ml}$, which determines the total probability of finding the electron, is often called the **atomic orbital.**

In eqn. (1.35), the wave function $\Psi(r,\theta,\phi)_{u,l,m_l}$ is expressed as a product of two functions, the radial part or radial function $R(r)_{n,l}$ and the angular part or angular wave function $Y(\theta,\phi)_{l,m_l}$. The radial wave function $R(r)_{n,j}$ shows how the wave function varies with $r$ keeping $\theta$ and $\phi$ constant. In other words, it represents the variation of $\Psi$ with $r$ in the same direction. The angular wave function $Y(\theta,\phi)_{l,m_l}$ is a joint function of $\theta$ and $\phi$ and it determines the nature of variation of $\Psi$ in different directions (determined by the magnitudes of $\theta$ and $\phi$) at a fixed radial distance, r. Thus, such a separation of the radial and the angular parts helps us to visualise the angular and radial dependence of the total wave function separately and independently of each other.

The expressions for the angular and the radial parts of the wave function of hydrogen atom (one-electron system), along with the corresponding symbols and the $n$, $l$ and $m_l$-values are given in the following table :

TABLE 1.10

| n | l | $m_l$ | Symbol | Angular wave function $Y(\theta,\phi)_{l,m_l}$ | Radial wave function $R(\mathrm{r})_{n,l}$ |
|---|---|---|---|---|---|
| 1 | 0 | 0 | 1$s$ | $\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$ | $2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\sigma/2}$ |
| 2 | 0 | 0 | 2$s$ | $\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$ | $2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}(2-\sigma)e^{-\sigma/2}$ |
| 2 | 1 | 0 | $2p_z$ | $\left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta$ | $\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \sigma e^{-\sigma/2}$ |
| 2 | 1 | +1 | $2p_y$ | $\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\sin\theta.\ \sin\phi$ | ” |
| 2 | 1 | −1 | $2p_x$ | $\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\sin\theta.\ \cos\phi$ | ” |

In this table : $\sigma=\frac{2Zr}{na_0}$ and $a_0=\frac{h^2}{4\pi^2me^2}$.

From the above table, it can be clearly seen that for any $s$-orbital (1$s$, 2$s$, 3$s$, 4$s$ etc.), the angular part of the wave function is always the same, irrespective of the principal quantum number $n$. The angular dependence of the $p$-orbital is also not influenced by the principal quantum number and this is also true for the $d$-orbitals.

*Radial dependence of wave functions : Graphical representation of radial distribution functions of the different orbitals* : The radial part $R(\mathrm{r})_{n,l}$ of the one-electron (hydrogen) wave function has no physical significance. However, its square $[R(r)_{n,l}]^2$ represents the probability of finding the electron in a small volume $dv$ close to the point where $R$ is measured. *The radial distribution function is a measure of the probability of finding the electron in a spherical shell of thickness dr at a distance r from the nucleus.* The volume corresponding to such a spherical shell is obtained by multiplying its surface area $4\pi r^2$ by $dr$. Hence, the probability of the electorn being present in the volume $4\pi r^2 dr$ is given by $4\pi r^2[R(r)_{n,l}]^2 dr$.

Putting the different values of $R(r)_{n,l}$ for the different $s$, $p$, $d$ and $f$-orbitals, the radial distribution functions for all these orbitals can be evaluated. The plots of the radial distribution function for the $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ orbitals are given in the following figures. The abscissa of the plots are drawn in units of $a_0$($a_0$=radius of maximum probability of the ground state orbital of hydrogen).

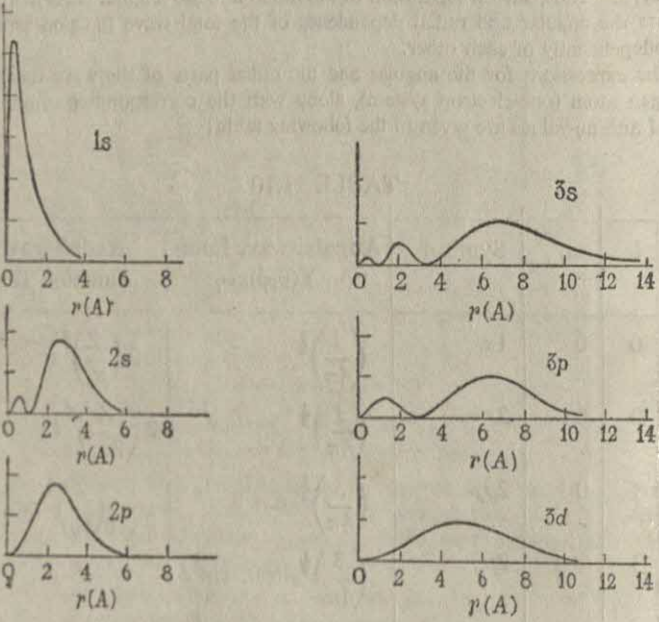

Fig. 1.25

It is clear from the figure that the probability of finding the electron at the nucleus is zero* and it is very small close to the nucleus. The maxima of these curves occur at distances where the probability of finding the electron is largest. This distance is often referred to as the **radius of maximum probability**. For the $1s$-orbital of hydrogen, the value of this radius of maximum probability is 0·529Å, which is exactly equal to the radius of the innermost stationary orbit of the Bohr-hydrogen atom. It can be noted from figures that, for the plots of $1s$, $2s$ and $3s$ orbitals, the radius of maximum probability increases significantly as the principal quantum number $n$ increases. Since, an electron which, on the average, is closer to the nucleus has a lower energy, the plots of $1s$, $2s$ and $3s$ indicate that the relative energy order of these orbitals is $1s < 2s < 3s$. Again, the plots of $2s$ and $2p$ as well as those of $3s$, $3p$ and $3d$ indicate that within any particular energy-shell defined by a particular principal quantum number $n$, the radius of maximum probability *decrease only slightly* as the subsidiary quantum number $l$ increases. It is to be noted also that, excepting the $1s$, $2p$, and $3d$ orbitals, which are the first members of each type of orbital, all the other orbitals have shell-like or layer structures like a set of concentric spheres.

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*As the nucleus is taken as the origin of the polar co-ordinate system, $r=0$ at the nucleus.

*Angular dependence of wave functions* : *Pictorial representation of the angular part of the wave function* $Y(\theta,\phi)_{l,m_l}$ *for various orbitals* : It has already been noted that, for a particular value of the principal quantum number, the extent of radial dependence of the wave functions on the different possible values of $l$ is rather small. But, the atomic orbitals are very much dependent on the angles $\theta$ and $\phi$, which actually define the geometry of the atom as a whole. Thus, for practical purposes.(where extreme accuracy is not essential), different types of orbitals in a particular energy-shell (like $3s$, $3p$ and $3d$) may be considered on the basis of their angular dependence only. From table 1.10, we see that the angular part of the wave function, $Y(\theta, \phi)_{l,ml}$, for the $s$-orbitals (for which $l=0$ and $m_l=0$) do not contain any term involving $\theta$ and/or $\phi$. So, the $s$-orbital is completely independent of angles $\theta$ and $\phi$. Hence, the wave function for $s$-orbital is spherically symmetrical. In contrast to the $s$-orbitals, the $p$-and the $d$-orbitals are not spherically symmetrical because, experssions for the radial part of their wave functions contain $\theta$ and/or $\phi$. They are very much dependent on the angles $\theta$ and $\phi$. The angular dependence of $p$-and $d$-orbitals are of different nature. The plots of the angular part of the wave functions, $Y(\theta,\phi)_{l,m_l}$ for the $2s$, $2p$ and $3d$ orbitals for a hydrogen atom (in polar coordinates) are given in figure 1.26.

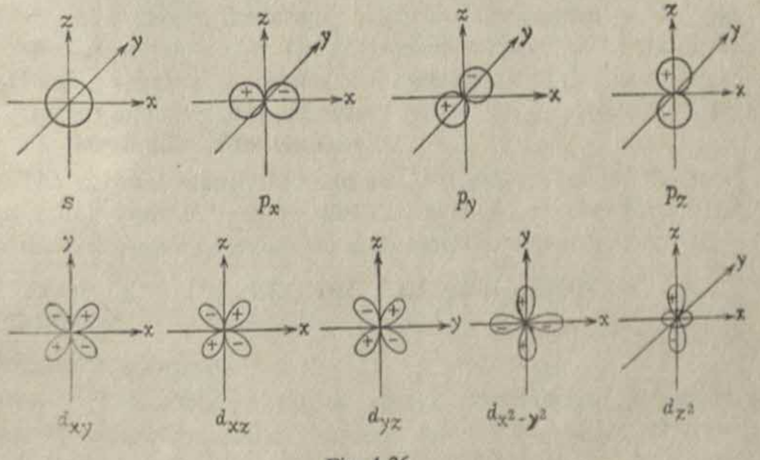

Fig. 1.26

**Relative importance of the radial part and the angular part of the wave functions for atomic orbitals** : To find the wave function accurately for a particular orbital, the relevant radial and angular parts are to be multiplied together. However, as already pointed out, the angular dependence of atomic orbitals (excepting the $s$-orbitals) is much greater in magnitude and significance compared to their radial part. Also, for the study and understanding of chemical bonding (which is perhaps the major objective in front of the chemists), the plots of angular dependence of wave function are found to be quite sufficient. Hence, a careful consideration of such plots of angular dependence of orbitals is much more important than a discussion on the exact geometrical pattern of these orbitals (taking into consideration the radial part) obtainable from contour plots.

**Sign of the plots of the angular part of the wave functions of different orbitals :** Fig. 1.26 shows that in the cases of *p*-and *d*-orbitals, the plots of the angular part of the corresponding wave functions contain+*ve* and -*ve* signs. The *p*-orbitals have +*ve* and −*ve* signs on opposite lobes *i.e.* on lobes above and below the nodal plane. Of the five *d*-orbitals, +*ve* and −*ve* signs are put on the alternate lobes in the cases of $d_{x^2-y^2}$, $d_{xy}$, $d_{xz}$ and $d_{yz}$, while for the $d_{z^2}$-orbital the two lobes along the *z*-axis contain +*ve* sign and the annular ring on the *X*-*Y*-plane contain−*ve* sign. The occurrence of different signs on different lobes originate from the difference in the nature of angular dependence in different quadrants of the co-ordinate system. These signs are related to the symmetry of the orbitals and the importance of these signs are realized during the study of chemical bonding when orbitals with indentical signs only can overlap with each other, leading to the formation of chemical bonds.

CHAPTER II

# PERIODIC CLASSIFICATION OF ELEMENTS
## OR
# CHEMICAL PERIODICITY

In the beginning of the 19th century, the domain of chemistry consisted of about 80 elements, together with a vast number of their compounds of various types. Chemistry, at that time, was a huge jumble of unrelated facts which were steadily increasing in volume and variety. It was an impossible task for an individual, or even for a group of individuals working together, to gain an overall grasp of this huge, diverse and apparently unrelated field of knowledge. A need was, therefore, felt to arrive at a natural classification of the chemical elements, which should be based on an inner relationship between some fundamental quantity, characteristic of each element and certain other properties of the elements. A further need was to recognise the periodicity in properties or chemical behaviour of elements which might be dependent on this fundamental quantity. Dalton's **atomic theory**, which recognized the atomic weight as a fundamental property of elements, threw open a new window through which light of new horizon poured in. The subsequent attempts to correlate the physical and chemical properties of the elements and their compounds with their atomic weights ultimately led to the formulation of **the periodic classification of the elements.**

The periodic classification of the elements is one of the most outstanding contributions to the development of chemistry. The usefulness of such a systematization cannot be over-emphasised.

## DEVELOPMENT OF PERIODIC CLASSIFICATION OF ELEMENTS.

### DOBEREINER'S TRIADS.

In 1829, J. W. Dobereiner of Germany observed that, among certain triads of chemically similar elements, the atomic weights increased regularly, *e.g.* Cl (35·5) : Br (80) : I (127).

The atomic weight of Br is nearly the average of those of Cl and I. Such a regularity was observed among the triads Ca (40), Sr (88) and Ba (137), as well as Li (7), Na (23) and K (39) and S (32), Se (79) and Te (127).

Or, in other words, the atomic weight of the middle element of such a *triad* was very nearly equal to the arithmetic mean of the weights of the other two elements.

## THE TELLURIC HELIX OF CHANCOURTOIS.

In 1862, de Chancourtois arranged the elements in the order of atomic weights (obtained by Cannizzaro's method) on a spiral line, wound around a cylinder in such a way that elements with similar properties stood one above another. The concept of periodicity found expression for the first time in this arrangement, but it received little attention and was soon forgotten.

## NEWLANDS' LAW OF OCTAVE.

In 1864, John Newlands of England arranged some of the elements known at that time in the increasing order of their atomic weights :

| | | | | | | |
|---|---|---|---|---|---|---|
| Li | Be | B | C | N | O | F |
| Na | Mg | Al | Si | P | S | Cl |

He noted that the eighth element starting from any one, is a kind of repeatition of the first, just like the eighth note in the octave of music. Thus, the properties of Li is repeated in Na and those of Be in Mg. Other such repeatitive pairs are B and Al, F and Cl *etc.* But, such a periodicity in properties was not observed when the elements beyond calcium (atomic weight=40) were so arranged.

## MENDELEYEV'S PERIODIC LAW.

**"The properties of the elements and their compounds are periodic functions of their atomic weights."** This famous **Periodic law** was put forward by the celebrated Russian chemist, Dimitri Ivanovitch Mendeleyev in 1869, and is the basis of **the periodic classification of elements** which is the corner-stone of modern chemistry. Julius Lothar Meyer, a German chemist, independently discovered the periodic law, but unfortunately his work went almost unnoticed at that time. Lothar Meyer focussed his attention on the periodic variation of some physical properties like atomic volume, melting point *etc.* with atomic weights, while Mendeleyev stressed on the periodic change of chemical properties of the atoms with the change in their atomic weights. Thus, both of Mendeleyev and Lothar Meyer used the atomic weight of the elements as the basis of their classifications.

Lothar Meyer observed (1870) that the atomic volume of elements (which is obtained by dividing atomic weight by density) changes periodically with the change of atomic weight. The curve obtained by plotting atomic volumes of the elements against their atomic weights is shown in Fig. 2.1. It is seen from the figure that the similar elements occupy similar positions in the curve. As for example, the alkali metals lie at the crests of the curve; the halogens lie at about the middle portion of the ascending loops, the alkaline earth metals at about the middle portion of the descending loops, the coinage metals near the bottom of the ascending loops, the metals of group VIII at about the bottom of the loops. On the basis of such observation, Lothar Meyer compiled a periodic table which was very similar to the one published by Mendeleyev.

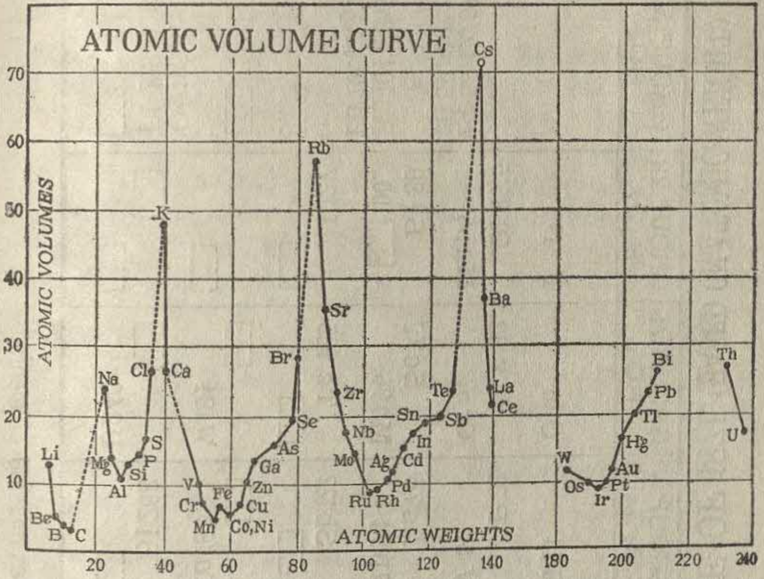

Fig. 2.1 : Lothar Meyer's curve

In his periodic table (Table 2.1), Mendeleyev arranged the then known elements in the order of increasing atomic weights in such a manner that similar elements were placed in the same **group** or vertical column. He even left some gaps in the table in order to ensure that similar elements are put in the same group. For this purpose he, in some cases, violated the principle of arranging the elements in the increasing order of the atomic weights, *i.e.* he placed Te before I though Te has an atomic weight greater than that of I. Later on, Moseley's work on the characteristic X-ray spectra of the elements led to the realisation that **the net positive charge on the nucleus** of an atom of any element, or the **atomic number**, is a property more fundamental than the atomic weight and under such consideration Mendelyev's reversal of the positions of Te and I was in order.

TABLE 2.1

### MENDELEYEV'S PERIODIC TABLE OF 1871. (BASED ON ATOMIC WEIGHT)

| SERIES | GROUP I $R_2O$ | GROUP II $RO$ | GROUP III $R_2O_3$ | GROUP IV $RO_2$ | GROUP V $R_2O_5$ | GROUP VI $RO_3$ | GROUP VII $R_2O_7$ | GROUP VIII $RO_4$ |
|---|---|---|---|---|---|---|---|---|
| 1 | H 1 | | | | | | | |
| 2 | Li 7 | Be 9·4 | B 11 | C 12 | N 14 | O 16 | F 19 | |
| 3 | Na 23 | Mg 24 | Al 27·3 | Si 28 | P 31 | S 32 | Cl 35·5 | |
| 4 | K 39 | Ca 40 | * □ 44 | Ti 48 | V 51 | Cr 52 | Mn 55 | Fe 56, Co 59<br>Ni 59, Cu 63 |
| 5 | (Cu 63) | Zn 65 | □ 68 | □ 72 | As 75 | Se 78 | Br 80 | |
| 6 | Rb 85 | Sr 87 | ?Y 88 | Zr 90 | Nb 94 | Mo 96 | * □ 100 | Ru 104, Rh 104<br>Pd 106, Ag 108 |
| 7 | (Ag 108) | Cd 112 | In 113 | Sn 118 | Sb 122 | Te 125 | I 127 | |
| 8 | Cs 133 | Ba 137 | ?Di 138 | ?Ce 140 | * ⬚ | ⬚ | ⬚ | ⬚ |
| 9 | * ⬚ | ⬚ | ⬚ | ⬚ | ⬚ | ⬚ | | ⬚ , ⬚ |
| 10 | ⬚ | ⬚ | ?Er 178 | ?La 180 | Ta 182 | W 184 | ⬚ | Os 195, Ir 197<br>Pt 198, Au 199 |
| 11 | (Au 199) | Hg 200 | Tl 204 | Pb 207 | Bi 208 | ⬚ | ⬚ | |
| 12 | ⬚ | ⬚ | ⬚ | Th 231 | ⬚ | U 240 | ⬚ | ⬚ |

* □ Indicates predicted elements, ⬚ Indicates missing elements.

N.B. At the time of 'Mendeleyev inert gases were unknown

### In search of a better base for periodic classification.

The periodic law, as put forward by Mendeleyev, was readily accepted by the scientific world, as it could successfully bring about a natural classification of the elements. But, with the arrangement of the elements in the increasing order of their atomic weights, difficulties arose with a few pair of elements such as cobalt and nickel, tellurium and iodine, thorium and protoactinium. It was found that, to obey the principle of periodicity of properties, their positions in the periodic table had to be reversed. In addition, the placement of each triad of elements at one place in Group VIII and that of the rare-earths at one room in Group III did not present a very satisfactory situation. It was, therefore, quite reasonable to believe that some other property of the atom, which was more fundamental in nature than the atomic weight itself, could be responsible for the periodicity of the physical and chemical properties of the elements and their compounds.

### Moseley's work on characteristic X-ray spectra of the elements : Origin of the concept of atomic number.

When cathode rays fall on a metal target (anticathode of an X-ray tube), X-rays, characteristic of the metal, are generated. Such **characteristic X-rays** were found to consist of groups of rays of different wavelengths denoted as K, L, M *etc.* series, depending on their energies,— the K-series being most energetic and common to all

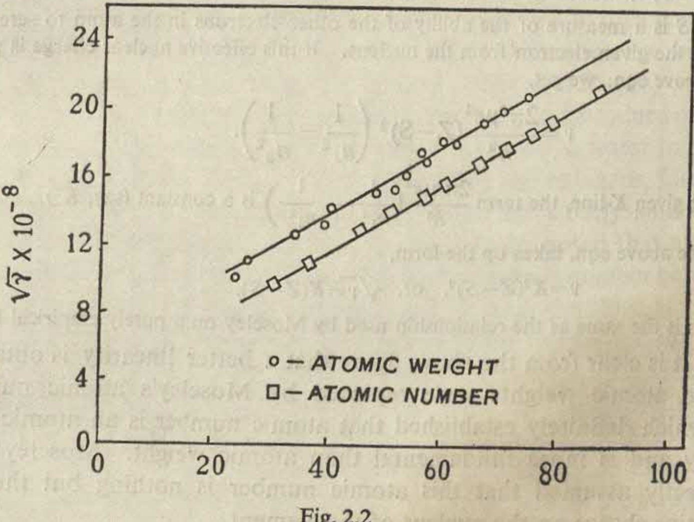

Fig. 2.2

elements. Moseley found out that the frequencies of any series of lines due to any particular metal, fit the relation,

$$\nu = C\,(Z-b)^2 \;\ldots\ldots\ldots (2.1)$$

where C and $b$ are constants and Z is an integer whose value increased regularly by one unit for successive elements in the periodic table. It was also noted that the value of Z coincided with the ordinal number of the element in the periodic table, and it was named **atomic number**. Moseley plotted $\sqrt{\nu}$ separately against atomic weight and atomic number Z, and obtained straight lines as shown in figure 2.2.

**Moseley's work in the light of Bohr's theory of the hydrogen atom.**

Moseley utilized the Bohr model of the hydrogen atom (see chapter I) to explain the relation between the frequency ($\nu$) and the atomic number ($Z$) represented by eqn. 2.1. It follows from the Bohr model that an X-ray may result from the transition of an electron from the $L$-shell to the $K$-shell.* According to Bohr, the frequency ($\nu$) in the emission spectrum of the hydrogen atom is represented by the eqn.,

$$\nu = \frac{2\pi^2 \mu e^4}{h^3} \cdot Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

where the different terms have their usual significance. In a multi-electron system (*i.e.*, in heavy elements), it is quite natural that the effective nuclear charge, as experienced by a given electron, would be less than the actual nuclear charge, $Ze$, due to the combined shielding effect of the other electrons lying between the nucleus and the given electron. The effective nuclear charge in such circumstances would be $(Z-S)\,e$, where $S$ is known as the *screening constant*.

$S$ is a measure of the ability of the other electrons in the atom to screen or shield the given electron from the nucleus. If this effective nuclear charge is put in the above eqn., we get,

$$\nu = \frac{2\pi^2 \mu e^4}{h^3} (Z-S)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

For a given $K$-line, the term $\dfrac{2\pi^2 \mu e^4}{h^3}\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$ is a constant (say, $K^2$).

So, the above eqn. takes up the form,

$$\nu = K^2 (Z-S)^2, \quad \text{or,} \quad \sqrt{\nu} = K(Z-S),$$

which is the same as the relationship used by Moseley on a purely empirical basis.

It is clear from the above figure that a better linearity is obtained when atomic weights were replaced by Moseley's atomic number Z, which definitely established that atomic number is an atomic property and is more fundamental than atomic weight. Moseley very correctly assumed that this atomic number is nothing but the net positive charge on the nucleus of the element.

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*X-rays can also be generated from the transition of electrons from $M$ and $N$-shells to the $K$-shell as well as such transitions from the $M$ and $N$-shells to the $L$-shell.

The periodic law was modified in this light as, **"the physical and chemical properties of the elements and their compounds are periodic functions of their atomic numbers."** A modified Mendeleyev periodic table in which the elements were arranged in the increasing order of their atomic numbers (Table 2.2) provided justification for some apparent anomalies in the original Mendeleyev Periodic Table, like the relative positions of the Co-Ni and Te-I pairs etc.

The horizontal rows of the periodic table are called **periods.** The first one is a **very short** period, containing only two elements H and He. The next two are **short** periods and contain 8 elements each, followed by two **long** periods consisting of 18 elements. The 6th period is a **very long** period of 32 elements and the last one is an incomplete period, containing mostly radioactive elements. The properties of the elements vary systematically along a period and will be discussed in details later.

The vertical columns of the table are called the **groups,** each group being sub-divided into two **sub-groups,** A and B. Elements of the same group are similar to each other in general characteristics, while the members of a particular sub-group are much more closely related to each other and are known as **congeners.**

The most important point to note here is that, the properties of the elements in a period or a group (and their compounds) do not change in a haphazard or arbitrary manner. They vary systematically with the atomic number, which is clearly reflected in the periodic recurrence of characteristic properties. Thus, the elements having atomic numbers 3 (Li), 11 (Na), 19 (K), 37 (Rb) and 55 (Cs) are all light, low-melting and soft metals, highly reactive, and produce oxides of the type $M_2O$ on exposure to air, which dissolve in water to yield the strongest alkalis. They react violently with the halogens, forming crystalline halides of the formula, MX which are closely similar to each other in most of their properties. It is to be noted that among the above-mentioned elements, the difference of atomic number between the first and the second and between second and the third is eight, and that between the third and the fourth and the fourth and the fifth is 18. These differences in atomic numbers correspond to the number of elements in the first two short periods (2nd and 3rd periods) and the two long periods (4th and 5th periods) to which these elements belong. Again, the elements with atomic numbers one unit less than the members of the above series, e.g. 2, 10, 18, 36, and 54 are all chemically inert and are all gaseous elements. These two series of elements show close similarity amongst themselves, but are quite different from other elements.

TABLE 2.2

## PERIODIC TABLE (BASED ON ATOMIC NUMBER) SHORT FORM
(MODERN VERSION OF MENDELEYEV'S PERIODIC TABLE

| PERIODS | SERIES | GROUPS | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | I A | I B | II A | II B | III A | III B | IV A | IV B | V A | V B | VI A | VI B | VII A | VII B | VIII | | | 0 | |
| 1 | 1 | 1·008<br>$_{1}$H | | | | | | | | | | | | | | | | | 4·003<br>$_{2}$He | 2 |
| 2 | 2 | 6·940<br>$_{3}$Li | | 9·013<br>$_{4}$Be | | | 10·82<br>$_{5}$B | | 12·011<br>$_{6}$C | | 14·008<br>$_{7}$N | | 16·000<br>$_{8}$O | | 19·00<br>$_{9}$F | | | | 20·18<br>$_{10}$Ne | 8 |
| 3 | 3 | 22·991<br>$_{11}$Na | | 24·32<br>$_{12}$Mg | | | 26·98<br>$_{13}$Al | | 28·09<br>$_{14}$Si | | 30·975<br>$_{15}$P | | 32·066<br>$_{16}$S | | 35·457<br>$_{17}$Cl | | | | 39·94<br>$_{18}$A | 8 |
| 4 | 4 | 39·100<br>$_{19}$K | | 40·08<br>$_{20}$Ca | | 44·96<br>$_{21}$Sc | | 47·90<br>$_{22}$Ti | | 50·95<br>$_{23}$V | | 52·01<br>$_{24}$Cr | | 54·94<br>$_{25}$Mn | | 55·85<br>$_{26}$Fe | 58·94<br>$_{27}$Co | 58·71<br>$_{28}$Ni | | 18 |
| | 5 | | 63·54<br>$_{29}$Cu | | 65·38<br>$_{30}$Zn | | 69·72<br>$_{31}$Ga | | 72·60<br>$_{32}$Ge | | 74·91<br>$_{33}$As | | 78·96<br>$_{34}$Se | | 79·916<br>$_{35}$Br | | | | 83·80<br>$_{36}$Kr | |
| 5 | 6 | 85·48<br>$_{37}$Rb | | 87·63<br>$_{38}$Sr | | 88·92<br>$_{39}$Y | | 91·22<br>$_{40}$Zr | | 92·91<br>$_{41}$Nb | | 95·95<br>$_{42}$Mo | | [99]<br>$_{43}$Tc | | 101·1<br>$_{44}$Ru | 102·91<br>$_{45}$Rh | 106·4<br>$_{46}$Pd | | 18 |
| | 7 | | 107·880<br>$_{47}$Ag | | 112·41<br>$_{48}$Cd | | 114·82<br>$_{49}$In | | 118·70<br>$_{50}$Sn | | 121·76<br>$_{51}$Sb | | 127·61<br>$_{52}$Te | | 126·91<br>$_{53}$I | | | | 131·3<br>$_{54}$Xe | |
| 6 | 8 | 132·91<br>$_{55}$Cs | | 137·36<br>$_{56}$Ba | | * 138·92<br>$_{57}$La | | 178·50<br>$_{72}$Hf | | 180·95<br>$_{73}$Ta | | 183·86<br>$_{74}$W | | 186·22<br>$_{75}$Re | | 190·2<br>$_{76}$Os | 192·2<br>$_{77}$Ir | 195·23<br>$_{78}$Pt | | 32 |
| | 9 | | 197·2<br>$_{79}$Au | | 200·61<br>$_{80}$Hg | | 204·39<br>$_{81}$Tl | | 207·21<br>$_{82}$Pb | | 209·0<br>$_{83}$Bi | | [210]<br>$_{84}$Po | | [210]<br>$_{85}$At | | | | [222]<br>$_{86}$Rn | |
| 7 | 10 | [223]<br>$_{87}$Fr | | 226·05<br>$_{88}$Ra | | ** [227]<br>$_{89}$Ac | | [257]<br>$_{104}$Ku | | [260]<br>$_{105}$Ha | INCOMPLETE PERIOD | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * LANTHANIDES<br>(Rare earth) | 140·13<br>$_{58}$Ce | 140·92<br>$_{59}$Pr | 144·27<br>$_{60}$Nd | [145]<br>$_{61}$Pm | 150·35<br>$_{62}$Sm | 152·0<br>$_{63}$Eu | 157·26<br>$_{64}$Gd | 158·93<br>$_{65}$Tb | 162·51<br>$_{66}$Dy | 164·94<br>$_{67}$Ho | 167·27<br>$_{68}$Er | 168·94<br>$_{69}$Tm | 173·04<br>$_{70}$Yb | 174·99<br>$_{71}$Lu |
| ** ACTINIDES | 232·05<br>$_{90}$Th | [231]<br>$_{91}$Pa | 238·07<br>$_{92}$U | [237]<br>$_{93}$Np | [242]<br>$_{94}$Pu | [243]<br>$_{95}$Am | [243]<br>$_{96}$Cm | [245]<br>$_{97}$Bk | [249]<br>$_{98}$Cf | [254]<br>$_{99}$Es | [253]<br>$_{100}$Fm | [256]<br>$_{101}$Md | [254]<br>$_{102}$No | [257]<br>$_{103}$Lw |

TRANSURANIUM ELEMENTS

**What is the best base of the periodic classification ?**

Uptil now we have found that both atomic weight and atomic number have been used as the basis of the periodic classification with considerable success. Though both of these are nuclear properties, the atomic number, in an indirect manner, is equal to the total number of electrons in the atom. Thus, it represents a nuclear as well as an extranuclear parameter of the atom.

Since many of the properties of the elements are primarily dependent on the extranuclear electrons, the atomic number is a better base for a periodic classification than the atomic weight. Still, atomic number cannot be considered to be the most appropriate basis for the periodic classification of elements, because of the fact that, different elements have different numbers of electrons arranged in the various energy-shells (*See Chapter I*). The outermost shells are of highest energy and are called the *valence-shell.* The electrons in this shell (valence-electrons) are most loosely bound and hence will be best available for chemical reactions. It is these valence-electrons that determine the chemical properties of the elements. Therefore, *the actual electronic configuration, especially that in the valence-shell, is the fundamental feature on which the ideal periodic table should be based.*

A periodic chart based on the electronic configuration of the elements is known as the **Bohr periodic table** or the **long form** of the periodic table and is shown in Table 2.3.

Like the modified Mendeleyev periodic chart (Table 2.2), it is also divided into seven horizontal rows or **periods**, but is vertically divided into eighteen columns or **groups**. Relation of this periodic table with the electronic configuration of the atoms will be discussed now. During this discussions, the figure (1.20), showing the order of filling up of different orbitals is to be always kept in mind.

In this periodic table, every period begins with an element having one electron in the *ns*-orbital or the valence-shell, where *n* is the principal quantum number of the outermost shell. Since the 1*s* orbital can accommodate only two electrons, the first period has only two members, *viz.* hydrogen and helium. The third electron in lithium, from which the second period begins, must go to the 2*s* orbital (see figures 1.19 and 1.20). Since there are one 2*s* and three 2*p* orbitals in the second energy-shell ($n=2$), each of which can accommodate two electrons, eight elements follow one another until all the 2*s* and 2*p* orbitals are completely filled up by electrons in neon ($2s^2\,2p^6$), which closes the second period. The third period also contains

TABLE 2.3

## PERIODIC TABLE (LONG FORM)

(BASED ON ATOMIC NUMBER)

| PERIODS ↓ | GROUPS | | | | | | | | | | | | | | | | | | NO. OF ELEMENTS IN THE PERIODS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\mathrm{I_A}$ | $\mathrm{II_A}$ | $\mathrm{III_A}$ | $\mathrm{IV_A}$ | $\mathrm{V_A}$ | $\mathrm{VI_A}$ | $\mathrm{VII_A}$ | VIII | | | $\mathrm{I_B}$ | $\mathrm{II_B}$ | $\mathrm{III_B}$ | $\mathrm{IV_B}$ | $\mathrm{V_B}$ | $\mathrm{VI_B}$ | $\mathrm{VII_B}$ | 0 | |
| | s-BLOCK ELEMENTS | | d-BLOCK ELEMENTS | | | | | | | | | | p-BLOCK ELEMENTS | | | | | | |
| 1<br>1s | 1 H 1·008 | | | | | | | | | | | | | | | | | 2 He 4·003 $1s^2$ | 2 |
| 2<br>2s 2p | 3 Li 6·939 | 4 Be 9·012 | | | | | | | | | | | 5 B 10·81 | 6 C 12·011 | 7 N 14·007 | 8 O 15·999 | 9 F 19·00 | 10 Ne 20·183 | 8 |
| 3<br>3s 3p | 11 Na 22·989 | 12 Mg 24·312 | TRANSITION ELEMENTS | | | | | | | | | | 13 Al 26·98 | 14 Si 28·086 | 15 P 30·974 | 16 S 32·064 | 17 Cl 35·453 | 18 A 39·948 | 8 |
| 4<br>4s 3d 4p | 19 K 39·102 | 20 Ca 40·08 | 21 Sc 44·956 | 22 Ti 47·90 | 23 V 50·942 | 24 Cr 52·00 | 25 Mn 54·94 | 26 Fe 55·85 | 27 Co 58·933 | 28 Ni 58·71 | 29 Cu 63·54 | 30 Zn 65·37 | 31 Ga 69·72 | 32 Ge 72·59 | 33 As 74·92 | 34 Se 78·96 | 35 Br 79·909 | 36 Kr 83·80 | 18 |
| 5<br>5s 4d 5p | 37 Rb 85·47 | 38 Sr 87·62 | 39 Y 88·905 | 40 Zr 91·22 | 41 Nb 92·91 | 42 Mo 95·94 | 43 Tc [99] | 44 Ru 101·07 | 45 Rh 102·905 | 46 Pd 106·4 | 47 Ag 107·87 | 48 Cd 112·40 | 49 In 114·82 | 50 Sn 118·69 | 51 Sb 121·75 | 52 Te 127·60 | 53 I 126·90 | 54 Xe 131·3 | 18 |
| 6<br>6s (4f) 5d 6p | 55 Cs 132·91 | 56 Ba 137·34 | 57 La* 138·91 | 72 Hf 178·49 | 73 Ta 180·948 | 74 W 183·85 | 75 Re 186·23 | 76 Os 190·2 | 77 Ir 192·20 | 78 Pt 195·09 | 79 Au 196·97 | 80 Hg 200·59 | 81 Tl 204·37 | 82 Pb 207·19 | 83 Bi 208·98 | 84 Po [210] | 85 At [210] | 86 Rn [222] | 32 |
| 7<br>7s (5f) 6d | 87 Fr [223] | 88 Ra [226] | 89 Ac** [227] | 104 Ku [257] | 105 Ha [260] | | | | | INCOMPLETE PERIOD | | | | | | | | | |

f-BLOCK ELEMENTS

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * LANTHANIDES (Rare earths) | 58 Ce 140·12 | 59 Pr 140·91 | 60 Nd 144·24 | 61 Pm [147] | 62 Sm 150·35 | 63 Eu 152·0 | 64 Gd 157·25 | 65 Tb 158·924 | 66 Dy 162·50 | 67 Ho 164·93 | 68 Er 167·26 | 69 Tm 168·934 | 70 Yb 173·04 | 71 Lu 174·97 |
| ** ACTINIDES | 90 Th 232·04 | 91 Pa [231] | 92 U 238·03 | 93 Np [237] | 94 Pu [242] | 95 Am [243] | 96 Cm [247] | 97 Bk [249] | 98 Cf [251] | 99 Es [254] | 100 Fm [253] | 101 Md [256] | 102 No [253] | 103 Lw [257] |

TRANSURANIUM ELEMENTS

eight elements, beginning with sodium with $3s^1$ configuration and ending when the 3*s* and 3*p* orbitals are filled up in argon ($3s^2 3p^6$).

After argon, a new period (the 4th period or the first long period) starts with potassium (atomic number=19). Since the 4*s* orbital has a lower energy than the 3*d* orbital, the 19th electron in potassium enters the 4*s* level. After the 4*s* orbital is filled up in calcium ($4s^2$), the subsequent electrons do not enter the 4*p* level which is of higher energy than the 3*d* level (see fig. 1.19). Thus, from scandium (atomic number=21), the electrons enter the five 3*d* orbitals which can accommodate a total of ten electrons. Thus, the transition elements, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel *etc.*, the *first series* of transition metals, enter the periodic table at this point. After the 3*d* levels are completely filled up, six more electrons enter and fill up the 4*p* levels to capacity and thus the fourth period is completed by eighteen members, the last one being krypton (atomic no.=36). In a similar manner 5*s*, 4*d* and 5*p* orbitals are filled up one after another in the fifth period which begins with rubidium (at. no.=37) and contains the second transition series [yttrium (39) to cadmium (48)] of elements and ends at xenon (atomic no.=54). The sixth period is the longest in the periodic table and is different from the others in that, in this period four orbitals lying in three different quantum levels (6*s*, 4*f*, 5*d* and 5*p*) are gradually filled upto their capacity. It begins with the filling up of the 6*s* orbital [cesium (55), barium (56)] and then a single electron enters the 5*d* orbital in lanthanum (57,$5d^1$). Thereafter, the 4*f* orbitals are progressively occupied. We have already noted in chapter I, that there are seven 4*f* orbitals, each of which can accommodate two electrons. So, altogether 14 electrons can reside in the 4*f* level corresponding to the 14 rare-earth elements constituting the first *inner transition series* and covering the atomic numbers 58—71. These elements are cerium (Ce, $4f^1$), praseodymium (Pr, $4f^2$), neodymium (Nd, $4f^3$,) promethium (Pm, $4f^4$), samarium (Sm, $4f^5$), europium (Eu, $4f^6$), gadolinium (Gd, $4f^7$), terbium Tb, $4f^8$), dysprosium (Dy, $4f^9$), holmium (Ho, $4f^{10}$), erbium (Er, $4f^{11}$), thulium (Tm, $4f^{12}$), yetterbium (Yb, $4f^{13}$), and lutetium (Lu, $4f^{14}$). These elements exhibit extreme similarity in most of their physical and chemical properties. After the rare-earths or the **lanthanide series** is completed in lutetium, the 5*d* orbitals are gradually filled up and the third series of transition elements appear. *This 3rd transition series* begins with lanthanum (57, $5d^1$), after which the 14 lanthanides have entered. After lutetium (71, $4f^{14}$), in hafnium (72, $5d^2$) the second electron enters the 5*d* orbital and the filling up of the 5*d* levels then gradually proceeds until the $5d^{10}$ cofiguration is attained in mercury (Hg, 80) and the 3rd transition series is thus completed. As is again evident from the Table 2.3, six elements [from thallium (81) to radon (86)] now appear and the 6th period is completed at radon, having $6s^2\ 6p^6$ configuration. The seventh and the last period begins with the filling of 7*s* orbital from francium (Fr, 87) and just as before, when one electron has entered the 6*d* orbital, the subsequent electrons enter the 5*f* orbitals and the periodic table ends with the second series of *inner transition elements* or the *actinides*, which are similar to the lanthanides in electronic configuration and properties.

In the 18 groups or columns of the Bohr periodic table, the members of each group possess the same *type of electronic configuration* in the valence-shell, as a result of which the elements belonging to a particular column or group have close similarity among themselves. There is also some chemical similarity among elements not belonging to the same group but having the same number of valence-electrons. Thus, the members of the group IIIB have three electrons in their valence-shells with $(n\text{-}1)d^1ns^2$ configuration, and they have some similarities with the aluminium group (Gr. III A) elements having $ns^2\ np^1$ configuration. Thus, the subgroups A and B of Gr. III show similarities amongst themselves, and this is generally true for all the groups. In the periodic table, the subgroups A and B are separated by three groups of triads labelled as Gr. VIII (Fe, Co, Ni ; Ru, Rh, Pd ; Os, Ir, Pt), which resemble each other closely. The 14 rare-earth elements and the members of the actinide series are placed in two seperate rows below the main body of the periodic table.

**Classification of elements in blocks.**

The elements arranged in the Bohr periodic table can also be classified into *s*-, *p*-, *d*-, and *f*-blocks . *The classification is based upon the designation of the orbital which receives the last electron.* Thus, the elements of Gr. IA and Gr. IIA (the alkali and the alkaline earth metals) receive their *last electron* (also called the *differentiating electron*) in the outermost *s*-orbital, having $ns^1$ and $ns^2$ configurations. These are called the *s*-block elements. The elements belonging to the groups IIIB, IVB, VB, VIB, VIIB and the inert gases (of Gr. O) receive their last electrons in the *np* orbitals, and hence are known as *p*-block elements.

The elements lying between *s*-and *p*-block elements have their outermost *s*-level filled up, and receive their last electron (the differentiating electron) in the *d*-orbitals of the penultimate (*n*-1) shell. These are the *d*-block or transition elements and comprise three series

[Scandium (21) to Zinc (30) ; Yttrium (39) to Cadmium (48) ; Lanthanum (57), Hafnium (72) to Mercury (80)], each having ten members corresponding to ten electrons gradually filling up the 3*d*, 4*d* and 5*d* orbitals. The type of electronic configuration in their valence-shell is generally $(n-1)d^{1-10}\,ns^2$*. Lastly, the elements in which the differentiating electrons are accomodated in the 4*f*, and the 5*f* orbitals are called the '*f*'-block elements. The 14 elements, in which filling up of the 4*f* orbitals takes place (the lanthanides), and the elements in which the 5*f* orbitals are filled up one by one (the actinides), are the members of the '*f*'-block elements and are generally characterised by the valence-shell configuration $(n-2)\,f^{1-14}\,(n-1)\,d^1ns^2$.

In another method of classification of elements based on electronic configuration in their valence-shell, the *s*-and *p*-block elements, taken together, are divided into (i) inert gas elements having $ns^2\ np^6$ configuration in the outermost shell and (ii) the representative elements having $ns^1$ to $ns^2np^5$ configurations. Thus, the lighter members of the Grs. IA, IIA and IIIB and those of IVB, VB, VIB and VIIB are the members of the representative elements. (iii) The *d*-block elements are called transition elements while (iv) the *f*-block elements are called the inner transition elements.

**Periodic properties of the elements.**

Most of the physical and chemical properties of the elements change periodically with their electronic configuration. The more important properties of this class are electrical conductivity (or metallic and non-metallic character), ionization energy or ionization potential, electron affinity, electronegativity, atomic and ionic radii, the possible oxidation states and the chemical properties of the oxides and the hydrides.

**Metallic and non-metallic character.**

On the basis of their electrical properties, elements can be classified into metals, metalloids and non-metals,. A substance is classified as a metal if its electrical conductivity is of the order of $10^4-10^5$ ohm$^{-1}$ cm$^{-1}$. A metalloid has a conductivity in the range $10^{-5}-10^1$ ohm$^{-1}$ cm$^{-1}$, and a non-metal has so high a resistance that it does not allow electricity to pass through it. The metallic elements (conductors) occur in the left hand side of the periodic table, while the non-metals (non-conductors or insulators) are found in the upper right-hand side, with the metalloids or semi metals placed in the middle of the periodic table between the two classes (Table 2.4). Thus, the electrical conductivity decreases with the gradual feeding of electrons in the valence-shell in the case of representative elements, the metalloids separating the conductors and the non-conductors. But, it must be noted here that, when an element exists in more than one allotropic forms, only one form fits into the trend of periodic variation, because the different forms have different structures and consequent different electrical properties. For example, amorphous carbon and diamond are non-conductors, while graphite is a good conductor of electricity. Inspite of this discrepancy, it is generally observed that, the members of the transition series, those of Gr. I, II and the heavier members of the Grs. IIIB, IVB, VB and VIB are metallic in character (Table 2.4). The non-metallic elements are the lighter members of Grs. IIIB, IVB, VB, VIB and VIIB.

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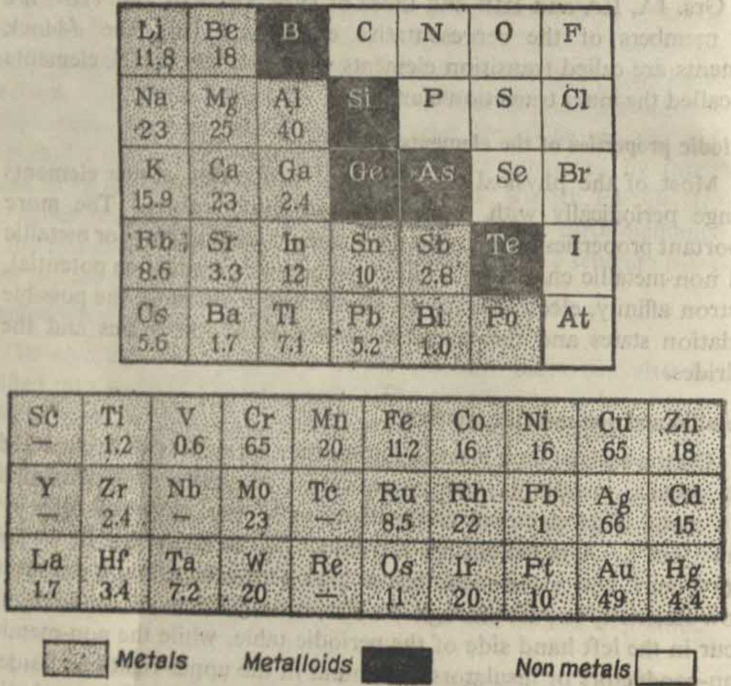
*Chromium ($Z=24$) and copper ($Z=29$) have $3d^5\ 4s^1$ and $3d^{10}\ 4s^1$ configurations respectively in their valence-shells.

TABLE 2.4



| | | | | | | |
|---|---|---|---|---|---|---|
| Li<br>11.8 | Be<br>18 | B | C | N | O | F |
| Na<br>23 | Mg<br>25 | Al<br>40 | Si | P | S | Cl |
| K<br>15.9 | Ca<br>23 | Ga<br>2.4 | Ge | As | Se | Br |
| Rb<br>8.6 | Sr<br>3.3 | In<br>12 | Sn<br>10 | Sb<br>2.8 | Te | I |
| Cs<br>5.6 | Ba<br>1.7 | Tl<br>7.1 | Pb<br>5.2 | Bi<br>1.0 | Po | At |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sc<br>— | Ti<br>1.2 | V<br>0.6 | Cr<br>65 | Mn<br>20 | Fe<br>11.2 | Co<br>16 | Ni<br>16 | Cu<br>65 | Zn<br>18 |
| Y<br>— | Zr<br>2.4 | Nb<br>— | Mo<br>23 | Tc<br>— | Ru<br>8.5 | Rh<br>22 | Pb<br>1 | Ag<br>66 | Cd<br>15 |
| La<br>1.7 | Hf<br>3.4 | Ta<br>7.2 | W<br>20 | Re<br>— | Os<br>11 | Ir<br>20 | Pt<br>10 | Au<br>49 | Hg<br>4.4 |

▨ *Metals*   *Metalloids* ■   *Non metals* ☐

Because of their comparatively large atomic volumes and low ionization potentials, the electrons of the metal atoms are rather free to move throughout the crystal of the metal under the influence of an applied potential difference and are very much available for the conduction of electricity resulting from the flow of electrons. In the non-metals, the electrons in the valence-shell are tightly bound due to the decrease in their atomic volume and hence are not available for electrical conduction. The metalloids are close to insulators with the outermost electrons fairly tightly bound, but tends to get loosened as the temperature is raised, allowing a small conduction of electricity through them.

In a particular group, the conductivity increases with the increase in atomic number. This is because of the creation of new electronic levels with increase in the value of the principal quantum number ($n$) and consequent increase in distance of the valence-shell electrons from the nucleus which make them more loosely bound.

**Ionization energy or ionization potential.**

The minimum energy required to completely remove the most loosely bound electron from a gaseous atom in its ground state to form a monopositive gaseous ion, leaving it without any kinetic energy,

$$M\ (g) \xrightarrow{+E_1 \text{ or } I_1} M^+\ (g) + e,$$

is the first ionization energy ($E_1$) which is usually measured in volts ($ev$) and is known as the first ionization potential $I_1$. It is an indication of the energy with which the atom in question binds its most loosely bound electron, and is a quantitative measure of the stability of the particular electronic configuration of the gaseous atom.[*] If the energy supplied to the gaseous atom is gradually increased, it is possible to cause the stepwise elimination of the second, third, fourth *etc.* electrons. The energy required for such elimination of electrons, $I_2$, $I_3$, $I_4$, are known as the 2nd, 3rd. 4th etc. ionization potentials respectively. The variation of ionization energies or ionization potentials follows the trend $I_1 < I_2 < I_3 \ldots . < I_n$.

**Factors influencing the magnitudes of ionization potentials.**

For comparative studies, the first ionization potentials are generally taken into consideration and the major factors that influence the magnitude of the first ionization potential are : (1) atomic size,

---

[*] The ionization potential in volts and ionization energy in electron volts are numerically same. This is the reason why these two terms are often used synonymously. However, for chemists, ionization energies are best represented in terms of kilo calories per gram-atomic weight, and the conversion factor from electron-volt to kilo calories per gram-atomic weight is 23.06.

(2) nuclear charge, (3) screening effect of the inner orbital electrons and (4) the extent of penetration of the outer electron into the charge-cloud created by the inner electrons.

These factors are related to each other : (1) Smaller the size of the atom, the more tightly are the outermost electrons bound and higher is the ionization energy. (2) Larger nuclear charge naturally results in a tighter binding of the outermost electrons, and hence, higher energy is required for ionization. (3) The inner shells of electrons screen the outermost electrons from the attraction of the positively charged nucleus, resulting in a loosening effect of the valence electrons, and this is known as the *screening effect*. The screening effect of the different orbitals with the same principal quantum number follows the trend $s>p>d>f$. (4) Due to the difference in the shape of the orbitals, an '$s$' orbital penetrates nearer the nucleus than the $p$-orbitals of the same the quantum level which, in turn, are more penetrating than the $d$-orbitals and the $d$-orbitals are more penetrating than the $f$-orbitals. If other factors remain identical, the ionization potentials follow the order, $s>p>d>f$. Variation of the first ionization potentials with atomic number is shown in Table 2.5. In any period the ionization potential increases with the increase in atomic number and becomes maximum at the inert gas having the "closed shell" of electrons. This

TABLE 2.5

| Element | Atomic No | $(I.P.)_1$ (e.v.) | Element | Atomic No. | $(I.P.)_1$ (e.v.) | Element | Atomic No. | $(I.P.)_1$ (e.v.) |
|---|---|---|---|---|---|---|---|---|
| H | 1 | 13·6 | Ca | 20 | 6·1 | Y | 39 | 6·4 |
| He | 2 | 24·6 | Sc | 21 | 6·5 | Zr | 40 | 6·8 |
| Li | 3 | 5·4 | Ti | 22 | 6·8 | N | 41 | 6·9 |
| Be | 4 | 9·3 | V | 23 | 6·7 | Mo | 42 | 7·1 |
| B | 5 | 8·3 | Cr | 24 | 6·8 | Tc | 43 | 7·3 |
| C | 6 | 11·3 | Mn | 25 | 7·4 | Ru | 44 | 7·4 |
| N | 7 | 14·5 | Fe | 26 | 7·9 | Rh | 45 | 7·5 |
| O | 8 | 13·6 | Co | 27 | 7·9 | Pd | 46 | 8·3 |
| F | 9 | 17·4 | Ni | 28 | 7·6 | Ag | 47 | 7·6 |
| Ne | 10 | 21·6 | Cu | 29 | 7·6 | Cd | 48 | 9·0 |
| Na | 11 | 5·1 | Zn | 30 | 9·4 | In | 49 | 5·8 |
| Mg | 12 | 7·6 | Ga | 31 | 6·0 | Sn | 50 | 7·3 |
| Al | 13 | 6·0 | Ge | 32 | 8·1 | Sb | 51 | 8·6 |
| Si | 14 | 8·2 | As | 33 | 9·8 | Te | 52 | 9·0 |
| P | 15 | 11·0 | Se | 34 | 9·8 | I | 53 | 10·5 |
| S | 16 | 10·4 | Br | 35 | 11·8 | Xe | 54 | 12·1 |
| Cl | 17 | 13·0 | Kr | 36 | 14·0 | Cs | 55 | 3·9 |
| Ar | 18 | 15·8 | Rb | 37 | 4·2 | Ba | 56 | 5·2 |
| K | 19 | 4·3 | Sr | 38 | 5·7 | | | |

happens due to the fact, in a particular period no new energy shell is created and the gradual addition of electrons in the same quantum level

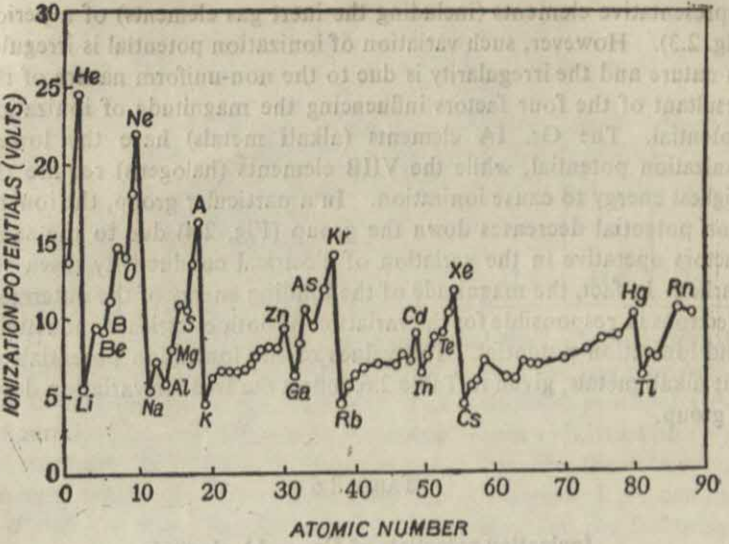


Fig. 2.3

along with the increase in nuclear charge results in a decrease in size. This decrease in size and increase in nuclear charge reinforce each

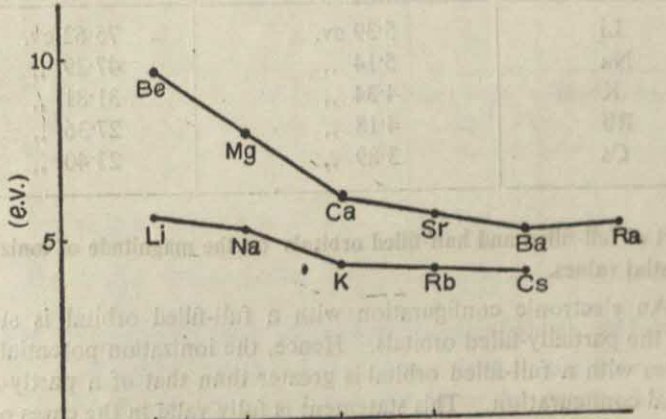


Fig. 2.4. Variation of ionization potential down the groups IA and IIA.

other and creates a stronger force of attraction on the outermost electrons and hence they require more energy to get ionized. Thus, parallelling the addition of electrons in the *ns*- and and *np*-levels upto the configuration $ns^2np^6$, the ionization potential increases among the representative elements (including the inert gas elements) of a period (fig. 2.3). However, such variation of ionization potential is irregular in nature and the irregularity is due to the non-uniform nature of the resultant of the four factors influencing the magnitude of ionization potential. The Gr. IA elements (alkali metals) have the lowest ionization potential, while the VIIB elements (halogens) require the highest energy to cause ionization. In a particular group, the ionization potential decreases down the group (Fig. 2.4) due to the same factors operative in the variation of electrical conductivity discussed earlier. In fact, the magnitude of the binding energy of the outermost electrons is responsible for the variation of both electrical conductivity and ionization potential. The values of the ionization potentials of the alkali metals, given in Table 2.6, reflect the trend in variation down a group.

TABLE 2.6

**Ionization potentials of Group IA elements.**

| Element | 1st I. P. | 2nd I. P. |
|---|---|---|
| Li | 5·39 ev. | 75·62 ev. |
| Na | 5·14 ,, | 47·29 ,, |
| K | 4·34 ,, | 31·81 ,, |
| Rb | 4·18 ,, | 27·36 ,, |
| Cs | 3·89 ,, | 23·40 ,, |

**Effect of full-filled and half-filled orbitals on the magnitude of ionization potential values.**

An electronic configuration with a full-filled orbital is stabler than the partially-filled orbitals. Hence, the ionization potential of a species with a full-filled orbital is greater than that of a partly-filled orbital configuration. This statement is fully valid in the cases of the representative elements as is evident from the data given in the table below, which show that the I. P. of neon with a $p^6$-configuration is much greater than any one of the elements with $p^1 - p^5$ configuration which precedes it.

TABLE 2.7

| Element | Li ($s^1$) | Be ($s^2$) | B ($p^1$) | C ($p^2$) | N ($p^3$) | O ($p^4$) | F ($p^5$) | Ne ($p^6$) |
|---|---|---|---|---|---|---|---|---|
| Ionization process | $Li \rightarrow Li^+$ | $Be \rightarrow Be^+$ | $B \rightarrow B^+$ | $C \rightarrow C^+$ | $N \rightarrow N^+$ | $O \rightarrow O^+$ | $F \rightarrow F^+$ | $Ne \rightarrow Ne^+$ |
| Ionization potential (ev) | 5·4 | 9·3 | 8·3 | 11·3 | 14·5 | 13·6 | 17·4 | 21·6 |

It is also evident from the above table that the half-filled orbital configuration have higher ionization potential than the less than half-filled configurations. Thus, nitrogen with half-filled *p*-orbital ($p^3$-configuration) has the highest I. P. among boron ($p^1$), carbon ($p^2$) and nitrogen ($p^3$). This is also generally true for the transition elements, where the $d^5$-configuration has the highest I. P. among $d^1$, $d^2$, $d^3$, $d^4$ and $d^5$-configurations as is shown in the following table.

TABLE 2.8

| Element | Sc | Ti | V | Cr | M |
|---|---|---|---|---|---|
| Ionization process | $Sc^{+2} \rightarrow Sc^{+3}$<br>($d^1$) | $Ti^{+2} \rightarrow Ti^{+3}$<br>($d^2$) | $V^{+2} \rightarrow V^{+3}$<br>($d^3$) | $Cr^{+2} \rightarrow Cr^{+3}$<br>($d^4$) | $Mn^{+2} \rightarrow Mn^{+3}$<br>($d^5$) |
| Ionization potential (ev) | 24·75 | 28·14 | 29·7 | 31·0 | 32·0 |

**Effect of charge on the nth ionization potential values of atoms and ions.**

For two ions (with non-inert gas configuration) of the same element, say $M^{+1}$ and $M^{+2}$, the energy involved in the process $M^0 \rightarrow M^+ + e$ is the first ionization potential. If the process $M^{+1} \rightarrow M^{+2} + e$ is to be brought about, a new factor, (in addition to all other factors influencing the first I. P.), *viz*. the over-all positive charge on the $M^{+1}$-ion, is brought into play. This factor tends to attract the valence-

TABLE 2.9

| Element with atomic number | Valence configuration of the atom | Successive ionization potentials (ev)* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $I_1$ | $I_2$ | $I_3$ | $I_4$ | $I_5$ | $I_6$ | $I_7$ | $I_8$ |
| Li (3) | $2s^1$ | 5·390 | 75·619 | | | | | | |
| Be (4) | $2s^2$ | 9·320 | 18·206 | 153·850 | | | | | |
| B (5) | $2s^22p^1$ | 8·296 | 25·149 | 37·920 | 259·298 | | | | |
| C (6) | $2s^22p^2$ | 11·264 | 24·376 | 47·864 | 64·476 | 391·986 | | | |
| N (7) | $2s^22p^3$ | 14·540 | 29·605 | 47·426 | 77·450 | 97·863 | 551·925 | | |
| O (8) | $2s^22p^4$ | 13·614 | 35·146 | 54·934 | 77·394 | 113·873 | 138·080 | 739·114 | |
| F (9) | $2s^22p^5$ | 17·42 | 34·980 | 62·646 | 87·230 | 114·214 | 157·117 | 185·139 | 953·600 |
| Ne (10) | $2s^22p^6$ | 21·559 | 41·070 | 64·000 | 97·160 | 126·400 | | | |

electron (which is to be removed) with a force greater than that operative in the case of the neutral atom $M^0$. This makes the value of the second ionization potential much higher than that of the first ionization potential. Thus, larger the positive charge on the positive ion which is to be further ionized, the greater is the magnitude of the ionization potential for the next ionization step. This is the reason why successive ionization potentials have progressively higher values.* The successive ionization potentials of a few elements are given in Table 2.9.

**Effect of closed-shell or inert gas configuration on the ionization potential values.**

A careful scrutiny of the data given in Table 2.9, shows that, after an ion reaches the closed-shell inert gas configuration (*e.g.* $ns^2$-configuration of helium or $ns^2\,np^6$-configuration of any other inert gas), the ionizaion potential value for the next ionization step (underlined figures in table 2.9) exhibits a steep jump. This happens because of the combined stabilizing effect of the filled orbital closed shell electronic configuration and the net positive charge on the species undergoing ionization.

**Electron affinity.**

When an electron is added to a gaseous atom X in its ground state, leading to the formation of a mononegative ion $X^-$,

$$X(g)+e \longrightarrow X^-(g)+\text{energy (EA)},$$

the energy (EA) released in that process is termed the electron affinity of the atom X. Thus, electron affinity is a measure of the attraction of the atom X for the electron. Thus, electron affinity of an element is of the same magnitude as that of the ionization potential of its mononegative ion, with opposite sign. The greater the magnitude of electron affinity, the greater is the power of the element to gain an electron. Electron affinity also reflects the oxidizing power of an element. If a second electron is to be added to the uninegative ion, forming a dinegative ion, the $X^-$ ion repels the incoming electron,

$$X^-(g)+e \longrightarrow X^{2-}+\text{Energy }(EA_2),$$

and so energy is required to force it in. Just like the 2nd ionization potential, this $EA_2$ is termed the 2nd electron affinity. This is the

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*It is better to point out here that ionization potential values greater than 15-16 *ev* are difficult to attain through normal chemical reactions. In some cases somewhat higher ionization potential values are attained because of very high lattice energy of the corresponding ionic compound produced. Many of the higher ionization potential values have been achieved in discharge tubes only. Hence, the formation of highly charged cations in chemical reaction is rather unlikely.

reason why the di-negative oxide ion $O^{2-}$ has a negative electron affinity. Electron affinity is very difficult to determine experimentally. This is best done from a Born-Haber cycle (see later). The electron affinities of only the most electronegative elements have been determined accordingly. Electron affinities of a number of elements in the periodic table is given in Table 2.10.

TABLE 2.10

**Electron affinities of some elements**

| | |
|---|---|
| $F \rightarrow F^-$ | 3·45 ev. |
| $Cl \rightarrow Cl^-$ | 3·61 ,, |
| $Br \rightarrow Br^-$ | 3·36 ,, |
| $I \rightarrow I^-$ | 3·06 ,, |
| $H \rightarrow H^-$ | 0·747 ,, |
| $O \rightarrow O^-$ | 1·47 ,, |
| $O \rightarrow O^=$ | −7·28 ,, |
| $S \rightarrow S^-$ | 2·07 ,, |
| $S \rightarrow S^=$ | —3·44 ,, |

**Factors influencing the magnitude of electron affinity.**

The major factors influencing electron affinity are (i) the size of the atom, (ii) the effective nuclear charge and (iii) the magnitude of charge on the ion concerned (when 2nd, 3rd etc. electron affinities are being considered). It is clear from the data in Table 2.10 that the electron affinity increases across a period from left to right. On moving across a period towards the right hand side, the atomic size decreases as the nuclear charge increases. With the increase of both the factors affecting electron affinity, the tendency of the atoms to attract an extra electron increases as a natural consequence. Thus, the electron affinities of the non-metals, which are at the right hand side of the periodic table, are high and that of the metals, which lie at the left hand side, are extremely low. Halogens (Gr. VIIB) have the highest electron affinities since, by acceptance of only one electron, their outermost electronic configuration of $ns^2np^5$ changes over to the extremely stable inert gas configuration $ns^2np^6$. But, the alkali metals, having $ns^1$ configuration overlying the $(n\text{-}1)\ s^2p^6$ inert gas configuration, have an overwhelming tendency to lose the $ns^1$ electron and hence acceptance of an electron by such a species is extremely improbable energetically. In a particular group, the electron affinity decreases downwards with the increase in atomic number due to the combined effect of the increase in atomic size and the screening effect, which overshadows the opposite effect due to the increase of nuclear charge.

It can be seen from the data presented in Table 2.10 that the electron affinity values of fluorine (3·45 ev) and oxygen (1·47 ev) (the first members of Gr VIIB and Gr VIB) are lower than the second members of the corresponding groups, *viz.* chlorine (3·61 ev) and sulphur (2·07 ev). This happens because the volume of the 2*p*-orbitals is much smaller than that of the 3*p*-orbitals (which are effective in the cases of Cl and S) and crowding of electrons in the relatively smaller volume of the 2*p*-orbitals results in a sharp increase of the inter-electron repulsion force in the case of the mononegative ions of fluorine and oxygen which decreases their electron affinity values below those of $Cl^-$ and $S^-$.

**Limitation of charge of an ion** : In chemical reactions leading to the formation of ionic compounds, the energy required to form the positive ions must be supplied by the release of energy in the system. The energy-releasing steps cannot provide more than 25-30 e.v. (600-700 kcals/mole) as a maximum. So, if the ionization energy required to produce an ion $M^{+n}$ is more than the above value, such an ion will not be formed under ordinary circumstances, and if the element is to form a compound in which it exhibits a valency of *n* units, the compound will be invariably covalent in nature—and not electrovalent. Such is the case with $BCl_3$. Although it seems probable that the boron atom will attain the stable electronic configuration of the preceding inert gas by forming $B^{+3}$ ion, the 3rd ionization potential of boron atom is 37·9 e.v., which is not available in a chemical reaction. So, boron reacts with excess of $Cl_2$ to produce covalent $BCl_3$. Similar is the case of $TiCl_4$, which is also covalent, a $Ti^{+4}$ ion cannot be formed in the reaction. In general, it is observed that the charge on a simple positive ion is limited to a maximum of three (provided the 3rd ionization potential is below 30 e.v.), even if an inert gas configuration is not reached. In a similar manner, the formation of negative ions with higher charges is also limited, since the additional electrons on the ions with lower charge are strongly opposed by the repulsion of the electrons already existing on the ion, and the repulsive force increases greatly with the gradual increase in the number of electrons on the ions. Thus, $Si^{-4}$ ions are not found in compounds, even though 4 electrons could be added to silicon ($3s^2\ 3p^2$ configuration) to attain the electronic configuration of the next higher inert gas. So, tetravalent silicon forms covalent compounds (with greater or lesser degree of polarity). But, in molecular ions like $SO_4^{-2}$, $CO_3^{-2}$ or $PO_4^{-3}$, the total negative charge is distributed over several atoms and repulsions between like charges are minimised. So, complex negative ions with very high charges may exist, if the charged molecule is large and the charges can be distributed over the molecule.

## Electronegativity.

If an atom A in a molecule AB has a stronger tendency to attract the shared electron-pair or bond-pair towards itself, as compared to that of the atom B, a polar covalent bond results in between A and B. This is represented as $\overset{\delta-\ \delta+}{\text{A—B}}$. In such cases, the atom A is said to be *more electronegative* than B. So, **electronegativity of an element is a measure of the power of an atom of that element to attract towards itself the pair of electrons (the bond-pair) holding it to another atom in a molecule or ion.** It is well-known that the ionization potential represents the attraction of the atom for its valence-electron and electron affinity determines its power of attracting electron from other atoms. Hence, magnitude of electronegativity of an element is essentially related to both ionization potential and electron affinity of the atom in question. It is to be realised that, although both electronegativity and electron affinity denote the electron-attracting property of an atom, **electronegativity is a property of an atom in the combined state** and *not* a property of the isolated atom itself, which is its electron affinity.

**Different electronegativity scales.**

A number of ways of computing electronegativities have been attempted. These are known as different electronegativity scales. The more well-known attempts to make quantitative evaluation of electronegativity are associated with Pauling, Mulliken, Allred and Rochow and to a lesser extent with the names of Gordy, Iczkowski, Margrave, and Klopman. It is obvious that, due to different environments of any particular atom in its various compounds, its electronegativity value cannot be constant, but for all practical purposes, it is assumed to be so.

**Pauling's scale of electronegativity.**

Pauling was the first to introduce a scale of electronegativity of atoms. His approach was based on the observed bond energy. *Bond energy is defined to be the energy required to break a chemical bond to get neutral atoms.* In most cases, bond energy can be determined experimentally. Pauling first suggested that the energy of *the purely covalent bond* in a molecule A—B is the arithmetic mean of the bond energies of the molecules A—A and B—B, *i.e.*

$$D_{A-B}\,(\text{expt.})=\tfrac{1}{2}(D_{A-A}+D_{B-B})=D_{A-B}\,(\text{calc.})\ldots\ldots(2{\cdot}2).$$

This is known as *the postulate of the additivity of covalent bonds.*

Let $X_A$ and $X_B$ represent the electronegativities of A and B respectively. So, when the bond A—B is purely covalent $X_A=X_B$. But, when A and B are dissimilar elements, $X_A \neq X_B$ and the bond in the molecule A—B develops some ionic character. If it is supposed that $X_A > X_B$, then the molecule AB may be represented as $\overset{\delta-}{A}\text{—}\overset{\delta+}{B}$, and greater amount of energy will be required to break this polar bond than what is required to break the corresponding bond in the purely covalent molecule A—B. In such cases, experimental bond energy, $D_{A-B}$ (expt.), will not be equal to $D_{A-B}$ (calc.), but it will be greater than that. This situation is mathematically represented as $[D_{A-B}\,(\text{expt.}) - D_{A-B}\,(\text{calc.})] = \Delta$ (where $\Delta$ is positive*.)

$$\text{or, } D_{A-B}\,(\text{expt.}) - \tfrac{1}{2}[D_{A-A} + D_{B-B}] = \Delta \ldots\ldots\ldots (2.3)$$

This indicates that, more energy is required to dissociate a bond with partial ionic character than the energy required to break the corresponding purely covalent bond. This $\Delta$ is a measure of the resonance energy due to the ionic character of the unsymmetrical bonds. $\Delta$ is also a measure of the electronegativity difference of the bonded atoms A and B and is proportional to $(X_A - X_B)$. The postulate of additivity of normal covalent bonds holds good for a large number of covalent molecules and the values of $\Delta$ can be utilised as a basis of formulating a scale of electronegativity of the elements.

Later on it was noticed that in the cases where the electronegativity differences between the combining elements are very large, the value of $\Delta$, calculated by using eqn. (2.3), is found to be negative and not positive or even zero. Such were the cases of the hydrides of the alkali metals. Pauling then proposed his famous *postulate of the geometric mean* to overcome this difficulty. This postulate states that, **the energy of a normal covalent bond between atoms A and B are equal to the geometric mean of $D_{A-A}$ and $D_{B-B}$**, *i.e.* the term $\tfrac{1}{2}[D_{A-A} + D_{B-B}]$ in eqn. (2.3) is to be replaced by $[D_{A-A} \times D_{B-B}]^{\frac{1}{2}}$.

Hence, eqn. (2.3) takes the final form,

$$[D_{A-B}\,(\text{expt.})] - [D_{A-A} \times D_{B-B}]^{\frac{1}{2}} = \Delta \ldots (2.4)$$

With this postulate, value of $\Delta$ assumes positive values in all cases. This is a more general relation which, under the conditions $X_A \simeq X_B$ virtually reduces to eqn. (2.3) because, under such conditions, $[D_{A-A} \times D_{B-B}]^{\frac{1}{2}}$ becomes equal to $\tfrac{1}{2}[D_{A-A} + D_{B-B}]$.

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*$\Delta$ is known as ionic-covalent resonance energy. From theoretical considerations, Pauling has shown that a mixture of ionic and covalent character results in a bond stronger than either of purely covalent or a purely ionic bond.

$\Delta$ values for the hydrogen halides and inter-halogen compounds of the type *XX′* are always found to be positive and lends experimental support to Pauling's idea expressed in the above equations.

As it is only possible to evaluate or determine the electronegativity difference (expressed in term of Δ) between the bonded atoms A and B, an electronegativity scale for all the elements can be formulated by fixing the electronegativity value of at least one element. From chemical stand-point, flourine is definitely the most electronegative element. Pauling assigned an electronegativity value of 4 to flourine and on that basis calculated the electronegativity values for all other elements using eqn. (2.4). TABLE 2.11 contains the electronegativity values of some elements in the Pauling scale.

TABLE 2.11

**Eletronegativities of some elements (Pauling's scale)**

| | | | | | | |
|---|---|---|---|---|---|---|
| Li | Be | B | C | N | O | F |
| 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4 |
| Na | Mg | Al | Si | P | S | Cl |
| 0.9 | 1.2 | 1.5 | 1.8 | 2.1 | 2.5 | 3.0 |
| K | Ca | Sc | Ge | As | Se | Br |
| 0.8 | 1.0 | 1.3 | 1.8 | 2.0 | 2.4 | 2.8 |
| Rb | Sr | Y | Sn | Sb | Te | I |
| 0.8 | 1.0 | 1.3 | 1.7 | 1.8 | 2.1 | 2·5 |
| Cs | Ba | | | | | |
| 0.7 | 0.9 | | | | | |

**Mulliken's scale of electronegativity.**

From theoretical considerations, Mulliken visualised electronegativity as the average of ionization potential and electron affinity. Mathematically, Mulliken's electronegativity of an element A is defined as

$$X_A = \frac{1}{2}(I_A + E_A)$$

where, $X_A$ =electronegativity of the element A in a molecule AB
$I_A$ =ionzation potential of A
$E_A$ =electron affinity of A.

Comparison of the data in TABLE 2.12 containing electronegativity values of certain elements in Mulliken's scale and Pauling's scale clearly shows that Mulliken's values are approximately 2·7 times the corresponding values in Pauling's scale. In other words, the electronegativity values in both these scales are proportional to each other.

The physical basis of this scale seems to be in order (as discussed earlier), as electronegativity is essentially related to both ionization potential and electron affinity. But, such a relation, though found to be reasonably valid in the cases of monovalent atoms, becomes largely inapplicable to polyvalent atoms.

TABLE 2.12

| Element | Ionization potential ($I_X$) (*ev*) | Electron affinity ($E_X$) (*ev*) | Mulliken's electronegativity $X_A = \frac{1}{2}(I_A + E_A)$ | $\frac{X_A}{2.7}$ | Pauling's Electro-negativity |
|---|---|---|---|---|---|
| F | 17.4 | 3.45 | 10.425 | 3.86 | 4.0 |
| Cl | 13.01 | 3.61 | 8.31 | 3.07 | 3.0 |
| Br | 11.84 | 3.36 | 7.6 | 2.81 | 2.8 |
| I | 10.45 | 3.06 | 6.755 | 2.50 | 2.5 |
| H | 13.59 | 0.75 | 7.17 | 2.65 | 2.1 |

Another difficulty of this scale is that, reliable electron affinity data for many atoms are not known and hence, calculation of electronegativity from Mulliken's formula cannot be made at all in those cases.

**Allred and Rochow's scale of electronegativity.**

More recently (in 1958), Allred and Rochow proposed a method for computing the electronegativities of elements. The idea behind this method is that, an atom attracts a valence-electron according to Coulombs law :

$$\text{Force of attraction, } F = \frac{(Z_{eff} \times e)\ (e)}{r^2} \qquad \ldots (2.5)$$

where, $Z_{eff}$ = effective nuclear charge felt by the valence-electron ;

$e$ = electronic charge

$r$ = covalent radius of the atom being considered.

The values of $Z_{eff}$, which can be calculated from the Slater rules (See page 83), takes into account the magnitude of screening effect of the inner electrons. Based on eqn. (2.5), the following mathe-

TABLE 2.13

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H<br>2.1 | | | | | | | | | | | | | | | | |
| Li<br>1.0<br>(0.98) | Be<br>1.5<br>(1.57) | | | | | | | | | | | B<br>2.0<br>(2.04) | C<br>2.5<br>(2.55) | N<br>3.1<br>(3.04) | O<br>3.5<br>(3.44) | F<br>4.1<br>(3.98) |
| Na<br>1.0<br>(0.93) | Mg<br>1.3<br>(1.0) | | | | | | | | | | | Al<br>1.5<br>(1.61) | Si<br>1.8<br>(1.90) | P<br>2.1<br>(2.19) | S<br>2.4<br>(2.58) | Cl<br>2.9<br>(3.16) |
| K<br>0.9<br>(0.82) | Ca<br>1.1<br>(1.0) | Sc<br>1.2<br>(1.36) | Ti<br>1.3<br>(1.54) | V<br>1.5<br>(1.63) | Cr<br>1.6<br>(1.66) | Mn<br>1.6<br>(1.55) | Fe<br>1.7<br>(1.83) | Co<br>1.7<br>(1.88) | Ni<br>1.8<br>(1.91) | Cu<br>1.8<br>(1.90) | Zn<br>1.7<br>(1.65) | Ga<br>1.8<br>(1.81) | Ge<br>2.0<br>(2.01) | As<br>2.2<br>(2.18) | Se<br>2.5<br>(2.55) | Br<br>2.8<br>(2.96) |
| Rb<br>0.9<br>(0.82) | Sr<br>1.0<br>(0.95) | Y<br>1.1<br>(1.22) | Zr<br>1.2<br>(1.33) | Nb<br>1.3 | Mo<br>1.3<br>(2.16) | Tc<br>1.4 | Ru<br>1.4 | Rh<br>1.5<br>(2.28) | Pd<br>1.4<br>(2.20) | Ag<br>1.4<br>(1.93) | Cd<br>1.5<br>(1.69) | In<br>1.5<br>(1.78) | Sn<br>1.7<br>(1.96) | Sb<br>1.8<br>(2.05) | Te<br>2.0 | I<br>2.2<br>(2.66) |
| Cs<br>0.9<br>(0.79) | Ba<br>0.9<br>0.89 | La<br>1.1 | Hf<br>1.2 | Ta<br>1.4 | W<br>1.4<br>(2.36) | Re<br>1.5 | Os<br>1.5 | Ir<br>1.6<br>(2.20) | Pt.<br>1.5<br>(2.28) | Au<br>1.4<br>(2.54) | Hg<br>1.5<br>(2.00) | Tl<br>1.5<br>(2.04) | Pb<br>1.6<br>(2.33) | Bi<br>1.7<br>(2.02) | Po<br>1.8 | At<br>2.0 |
| Fr<br>0.9 | Ra<br>0.9 | Ac<br>1.0 | | | | | | | | | | | | | | |

matical relationship between the Allred-Rochow and the Pauling scale has been developed. Electronegativity in the Allred-Rochow scale ($X_{AR}$) can be calculated from the relation

$$X_{AR}=0.359\frac{Z_{eff}}{r^2}+0.744 \qquad \ldots(2.6)$$

The numerical constants are chosen to obtain electronegativity values in the range of the Pauling scale.* In Table 2.13, the electronegativity values in the Allred-Rochow and the Pauling scales (the values in parenthesis represent those in the Pauling scale) are shown.

**Atomic volume.**

In 1870, Lother Meyer noticed that the plot of atomic volume against atomic weight is periodic in nature (see fig. 2.1). The figure clearly shows that along with the change of their atomic weights the atomic volumes of the elements undergo a periodic variation. The atomic volume, which represent the volume occupied by $6.023\times10^{23}$ atoms also roughly indicate relative volumes of the individual atoms. But such volumes are not always constant and were found to depend on various factors like state of aggregation, crystal structure, temperature of measurement etc. It was also recognized that, compared to the atomic volumes, the corresponding atomic radii are less dependent on the factors mentioned before. Again, the volume of an atom, being a function of its radius, the horizontal and vertical variation of atomic volume should closely follow the pattern of variation of atomic radii. Hence, the discussion on atomic radii which immediately follows takes adequate care of the atomic volume factor. However, it must be recognised that the concept of periodic variation of atomic volume with the change in atomic weight is very useful in understanding the chemistry of the elements. It can also account for the periodic variation of many properties of the elements either along a period or up and down a particular group.

**Atomic and covalent radii.**

It is quite obvious that it is not possible to isolate an individual atom and determine its volume or radius. The atomic volume or radius has to be determined under conditions in which the atom in question must be present in its natural surrounding either as the free element or in the covalently bonded state in one of its compounds.

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*The most serious disadvantage of this very convenient method is the unreliable values for the covalent radii of atoms.

It has been recognised that the size of an atom of the free element is identical with that of the same atom in one of its purely covalent compounds. This is the reason why the two terms **atomic radius** and **covalent radius** are used synonymously.

According to the wave mechanical model of the atom, no atom can have a rigidly defined volume or radius. But, from X-ray studies of pure elements and their compounds, it has been found that the atoms (and ions) do behave like hard spheres having a more or less definite radius within which most of its electron density is located. So, if the distance of the closest approach of two such atoms of the same element behaving as hard spheres be taken as $d$, $d/2$ will represent the atomic radius that can be used for practical purposes. Such a radius, assigned to a neutral atom present in the elementary state or to an atom present in one of its purely covalent compounds, is known as the atomic radius of the element being considered. The best method for the determination of atomic radii of elements is the method of X-ray analysis of the crystals* of elements (see chapter VIII for the principle of this method). Other methods like electron and neutron diffraction and band spectroscopy can also furnish quite reliable data for the inter-nuclear distances in free elements and covalent molecules.

### Bond length of covalent molecules and atomic radii of the bonded atoms.

For elements forming diatomic molecules like $X_2$ (e.g. $Cl_2$, $Br_2$, $I_2$ etc.), a shared electron pair or a covalent single bond holds the two atoms together and the distance between the nuclei of the two atoms of the molecule is termed the **bond length.** One half of this bond length (previously denoted as $d$) is called the covalent radius or atomic radius of the element X. For a heteronuclear covalent molecule like AX, the inter-nuclear distance between A and X (i.e., the bond length) determined by any one of the above methods, is to be apportioned properly so as to arrive at the correct atomic radii of A and X. This can be done successfully only if the atomic radius of either A or X is found out experimentally by the study of another system containing A or X, or a reasonable value for the radius be assigned to one of them. For example, the Si—C bond length in tetramethyl silane, $(CH_3)_4$ Si, is experimentally found to be 1.93Å. Also the experimental value for the atomic radius of silicon ($r_{si}$), as determined by the X-ray analysis of pure silicon crystals, is 1.17 Å. Hence, the atomic radius of carbon ($r_c$) should be $(1.93-1.17)\mathring{A}=0.76\mathring{A}$. This value is very close to the $r_c$ value of $0.77\mathring{A}$ obtained by the X-ray analysis of diamond. Similarly, if the atomic radii of two elements are known, then the bond length holding them together in a covalent moleculs can be calculated by just adding up the two radii. Thus, if it is known that $r_c=0.77$ and $r_{Si}=1.17$, then the Si—C bond length should be $(1.17+0.77)\mathring{A}=1.94\mathring{A}$, which agrees well with the experimental value of $1.93\mathring{A}$.

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*Such measurements, however, do not represent the actual extension of atoms or ions. These actually give a measure of the distance to which the centres of the atoms or ions can approach one another in the crystal.

**Factors influencing the magnitude of atomic and covalent radii.**

While considering the magnitudes of the atomic or covalent radii values one must keep in mind that, many factors, such as bond order (*i.e.* single or multiple bonds), degree of ionic or covalent character of the bond, structure of the molecule, oxidation state of the atoms in question, even the different allotropic modifications of the same element affect such calculations. Atomic radii are, therefore, often designated as tetrahedral, octahedral or planar radii, ionic radii *etc.*

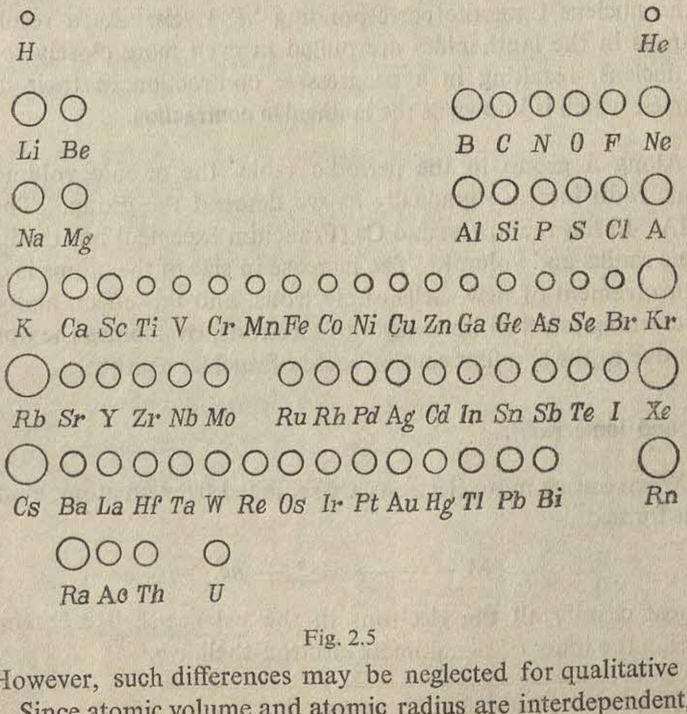
H
He
Li Be
B C N O F Ne
Na Mg
Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Rn
Ra Ac Th U

Fig. 2.5

However, such differences may be neglected for qualitative purposes. Since atomic volume and atomic radius are interdependent, the periodic variation of the atomic radii and the atomic volume follows, the same trend as is shown in fig. 2.5.

Thus, the atomic radii and atomic volume decreases from left to right across a period. Leaving aside the inert gas elements, the Gr. IA elements (the alkali metals) have the largest atomic radii and atomic volume, while the Gr. VIIB elements, the halogens, possess the lowest atomic volumes and atomic radii. This happens because of the fact that, in a given period, the successive electrons are added to the same energy-shell and hence are drawn close towards the nucleus with the increase in the nuclear charge. This results in a decrease in atomic volume and atomic radius. Such decrease in atomic volume is less marked among the transition elements. Here the last electrons are fed into a '*d*' level located in an inner energy-shell and should have been pulled in more closely. But, the mutual repulsion of the *d*-electrons counteracts this effect considerably and hence the decrease in atomic volumes of the transition elements are not so pronounced. The most profund effect in the decrease of atomic radius is found in the inner transition elements or the lanthanide series, where the last electrons are accommodated in an '*f*' orbital situated even more close to the nucleus than the corresponding '*d*' levels. As a result, the electrons in the lanthanides are pulled in even more closely towards the nucleus, resulting in a progressive contraction in their atomic volumes, which is known as the **lanthanide contraction.**

Along a group in the periodic table, the atomic volume and atomic radii increase gradually as we descend the group. Thus, in Gr. IA, Li has the lowest and Cs (Francium excepted) has the highest atomic radius and volume. The increase in size of the atoms is due to the involvement of new shells of electrons, and this effect, along with the screening effect of inner layer of electrons, overcomes the opposite effect due to the simultaneous increase of nuclear charge.

**Ions and ionic radii.**

When one or more electrons are removed from an atom, a positive ion is formed.

$$M \longrightarrow M^{+n} + ne.$$

In most cases*, all the electrons in the valence-shell are removed, exposing the inner or penultimate electron-shell, *e.g.*

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*Exceptions are found in Tl, Sn, Pb etc.

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e$$

$$\boxed{\mathrm{Ne}}\; 3s^1 \qquad \boxed{\mathrm{Ne}}$$

$$\mathrm{Mg} \longrightarrow \mathrm{Mg}^{++} + 2e$$

$$\boxed{\mathrm{Ne}}\; 3s^2 \qquad \boxed{\mathrm{Ne}}$$

As the first inner shell (called the penultimate shell) is of much smaller size than the outermost valence-shell (due to its principal quantum number being one unit less), the positive ion (cation) is smaller than the corresponding atom. Again, due to the loss of electrons, the net positive charge becomes greater than the net negative charge due to the orbital electrons. This increase in resultant positive charge pulls in the outer electron layers, resulting in a contraction of size. The following illustrations will bear out this conclusion :

Atomic radius of Li $= 1.34$ Å
Ionic radius of $Li^+$ $= 0.68$ Å
Atomic radius of Al $= 1.18$ Å
Ionic radius of $Al^{+3}$ $= 0.50$ Å

When one or more electrons are added to an atom, a negative ion (anion) is formed :

$$\mathrm{M} + ne \longrightarrow \mathrm{M}^{-n}$$

Here, the net negative charge exceeds the nuclear positive charge and, as a result, the electrons are held more loosely and the electron cloud expands due to mutual repulsion, resulting in the larger size of a negative ion than the parent atom. Two concrete examples are given below :

Atomic radius of Cl $= 0.99$ Å
Ionic radius of $Cl^-$ $= 1.81$ Å
Atomic radius of O $= 0.73$ Å
Ionic radius of $O^{2-}$ $= 1.40$ Å

This effect is pictorially represented in fig. 2.6.

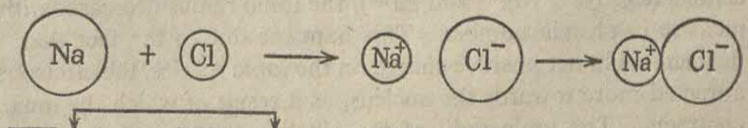

Fig. 2.6

Thus, the negative ion is invariably larger than the parent atom. The ionic radii of some cations (in their usual oxidation states) are given in table 2.14.

TABLE 2.14

| Ion | Ionic radius Å | Ion | Ionic radius Å | Ion | Ionic radius Å |
|---|---|---|---|---|---|
| $Li^+$ | 0.68 | $Be^{+2}$ | 0.31 | $Mn^{+2}$ | 0.80 |
| $Na^+$ | 0.95 | $Mg^{+2}$ | 0.65 | $Fe^{+2}$ | 0.76 |
| $K^+$ | 1.33 | $Ca^{+2}$ | 0.99 | $Co^{+2}$ | 0.74 |
| $Rb^+$ | 1.48 | $Sr^{+2}$ | 1.13 | $Ni^{+2}$ | 0.69 |
| $Cs^+$ | 1.69 | $Ba^{+2}$ | 1.35 | $Cu^{+2}$ | 0.72 |
| $Cu^+$ | 0.96 | $Zn^{+2}$ | 0.74 | $B^{+3}$ | 0.20 |
| $Ag^+$ | 1.26 | $Cd^{+2}$ | 0.97 | $Al^{+3}$ | 0.50 |
| $Au^+$ | 1.36 | $Hg^{+2}$ | 1.10 | $Ga^{+3}$ | 0.62 |
|  |  |  |  | $In^{+3}$ | 0.81 |
| $Tl^+$ | 1.44 |  |  | $Tl^{+3}$ | 0.91 |
|  |  |  |  | $Fe^{+3}$ | 0.64 |
|  |  |  |  | $Cr^{+3}$ | 0.63 |

It has been observed that, (i) for the elements of the same period, the radii of the cations are smaller than the anions. This happens because, (*a*) the cations are formed by the loss of outermost electron(s) and consequent reduction in size and (*b*) the excess nuclear positive charge further contracts the outer orbitals. (ii) In the case of the anions, the reverse effect takes places, because the crowding of the incoming electrons in the outermost orbital and consequent inter-electronic repulsion coupled with the lossening of the outer electrons due to greater orbital negative charge which exceeds the nuclear positive charge by one or more units. (iii) In a particular group of elements, the ionic radius increases with the increase in atomic number. For a series of ions having the same number of electrons *i.e.*, isoelectronic cations (*e.g.* $Na^+$, $Mg^{+2}$ and $Al^{+3}$), the ionic radius decreases with the increase in atomic number. This happens due to the fact that, with the increase in net positive charge on the ionic species, the electrons are attracted more towards the nucleus, as a result of which the ionic size contracts. The ionic radii of the alkali metal cations increase at a slower rate after $K^+$. This happens because there occurs, in between potassium and rubidium, the first transition series, and as the differentiating electrons in the transition elements enter the inner '*d*'-level, the increased nuclear charge acts strongly on them and results in contraction of their size, which has its effect on the ionic radii of the atoms of the subsequent elements. (iv) The ions of the elements of any particular transition series, in a particular oxidation state, exhibit a slight decrease in radius along with increase in their atomic numbers. This is clearly reflected in the data included in the Table 2·15 given below.

TABLE 2.15

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $Sc^{+3}$ | $T^{+3}$ | $V^{+3}$ | $Cr^{+3}$ | $Mn^{+3}$ | $Fe^{+3}$ | $Co^{+3}$ | | |
| 0.81Å | 0.76Å | 0.74Å | 0.69Å | 0.66Å | 0.64Å | 0.63Å | — | — |
| | $T_i^{+2}$ | $V^{+2}$ | $Cr^{+2}$ | $Mn^{+2}$ | $Fe^{+2}$ | $Co^{+2}$ | $Ni^{+2}$ | $Cu^{+2}$ |
| — | 0.90Å | 0.84Å | 0.84Å | 0.80Å | 0.76Å | 0.74Å | 0.69Å | 0.72Å |

The most striking evidence of the decrease in ionic radii is seen in the case of the lanthanide elements in their most stable oxidation state, +3, as is evident from the data given in Table 2.16.

TABLE 2.16

| | | | |
|---|---|---|---|
| $La^{+3}$ | 1.061Å | $Tb^{+3}$ | 0.923Å |
| $Ce^{+3}$ | 1.034 ,, | $Dy^{+3}$ | 0.908 ,, |
| $Pr^{+3}$ | 1.013 ,, | $Ho^{+3}$ | 0.894 ,, |
| $Nd^{+3}$ | 0.995 ,, | $Er^{+3}$ | 0.881 ,, |
| $Pm^{+3}$ | 0.979 ,, | $Tm^{+3}$ | 0.869 ,, |
| $Sm^{+3}$ | 0.964 ,, | $Yb^{+3}$ | 0.858 ,, |
| $Eu^{+3}$ | 0.950 ,, | $Lu^{+3}$ | 0.848 ,, |
| $Gd^{+3}$ | 0·938 ,, | | |

This contraction is responsible for certain special features of the chemistry of the third transition series of elements that follows the lanthanides in the periodic table. The problem of separation of zirconium and hafnium and of niobium and tantalum appears because the radii of these pairs of atoms are very near to each other due to the interposition of the lanthanide elements between the 2nd and the 3rd transition series.

**Determination of Ionic radii.**

It is well-known that chemically similar atoms do not form ionic compounds and hence, the radii of the ions cannot be determined by measuring the inter-nuclear distance of a molecule $A_2$ and dividing it by 2. Also, creation of isolated ions for the study of their physical properties like size or radius is extremely difficult, if not impossible. Hence it must be remembered that, the ionic radii values cited before are the radii of the ions in ionic crystals. Ions are generally regarded as rigid spheres* and they are usually packed as closely as possible in three dimensional array. In an ionic crystal a particular type of ion is surrounded by the maximum possible number of ions of opposite sign and this number is known as the coordination number of that particular ion. The exact value of this coordination number generally depends on the cation : anion ratio ($r^+/r^-$) of the component ions of the ionic crystal and the value of this radius-ratio gives an idea about the probable arrangement of the anions around the cations in a particular ionic crystal. This is clearly illustrated by the informations included in the following table.

TABLE 2.17

| Radius ratio ($r^+/r^-$) | Coordination number | Coordination geometry | Some examples |
|---|---|---|---|
| Upto 0.15 | 2 | linear | |
| 0.15—0.22 | 3 | triangular | |
| 0.22—0.41 | 4 | tetrahedral | $CaF_2$, $Na_2O$, ZnS<br>$BaCl_2$, $K_2O$, $K_2S$ |
| 0.41—0.73 | 4 | Planar | |
| 0.41—0.73 | 6 | octahedral | $Al_2O_3$, $Fe_2O_3$,<br>$Cr_2O_3$ |
| Greater than 0.73 | 8 | cubic | NaCl, KCl, CsF,<br>MgO, CaS, CdO,<br>PbS |

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*We say *generally* because the ions are not *actually* rigid spheres as they do change their size to some extent depending on their coordination numbers. The values of the ionic radii generally quoted in the literature as crystal radii are those for a coordination number of 6.

In a solid ionic compound, the internuclear distance ($d_{a-b}$) between the two oppositely charged ions packed together within the crystal lattice (see fig. 2.7 below) can be determined by X-ray analysis of the crystal as well as by neutron deffraction and electron deffraction techniques. Of these methods, the X-ray deffraction technique, using single crystals of ionic compounds, is most widely used for the determination of internuclear distance. Thus, such an internuclear distance, determined by X-ray deffraction method, is equal to the sum of the cation radius and the anion radius, *i.e.* $d_{A-B} = r^+ + r^-$. Hence, the problem of determination of the radii of the individual ions is now reduced to the one of apportioning this internuclear distance properly to the anion and the cation. Quite a number of methods have been proposed from time to time to achieve this purpose. Of these methods, *Lande's method* and *Pauling's method* are the more important ones and Pauling's method is considered to be the best by the chemists.

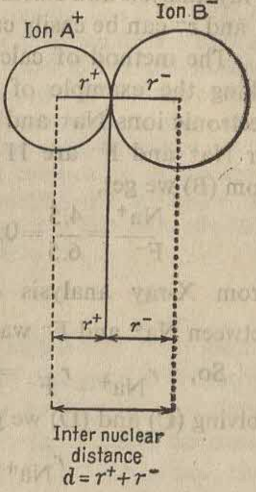

Fig. 2.7

Pauling's method is based on two assumptions : (i) the cation $A^+$ and the anion $B^-$ of the ionic crystal $A^+B^-$ are in contact with each other so that the internuclear distance of the two ions is equal to the sum of the radii of the cation ($r^+$) and the anion ($r^-$); (ii) The ionic radii of isoelectronic ions with inert gas configuration ($r^+$ and $r^-$) are inversely proportional to the effective nuclear charge $Z_{eff}$;

$$i.e., \quad r^{\pm} = \frac{C_n}{Z_{eff}} = \frac{C_n}{(Z-S)} \quad .. \quad (A)$$

where, $Z$=atomic number, $S$ is the screening constant of the ion and $C_n$ is a constant which depends on the principal quantum number of the outermost electrons. Thus, for two isoelectronic ions (like $Na^+$ and $F^-$),

$$\frac{r^+}{r^-} = \frac{(Z_{eff})^-}{(Z_{eff})^+} \quad .. \quad (B)$$

Pauling took into consideration the internuclear distance of several ionic compounds containing isoelectronic ions like NaF, KCl, RbBr, CsI, in all of which most of the factors that affect the ionic size remain constant for all practical purposes, and the radius ratios $r^+/r^-$ are all almost equal and have a value of $\sim$0.75. The values of

$Z_{eff}=(Z-S)$ were calculated using Slater's rule[1],[2] and the value $r^+/r^-$ was obtained. Thus, after determining the value of $d_{A-B}=r^++r^-$ by X-ray analysis and calculating the $r^+/r^-$ value, the individual values of $r^+$ and $r^-$ can be easily calculated.

The method of calculation used by Pauling can be illustrated by taking the example of NaF. The screening constant for the isoelectronic ions $Na^+$ and $F^-$ is 4.5. Thus, the effective nuclear charge for $Na^+$ and $F^-$ are $11-4.5=6.5$ and $9-4.5=4.5$ respectively. So, from (B) we get,

$$\frac{Na^+}{F^-}=\frac{4.5}{6.5}=0.699 \simeq 0.70 \ldots\ldots\ldots (C)$$

From X-ray analysis of NaF crystals, the internuclear distance between $Na^+$ and $F^-$ was found to be 2.31Å,

$$\text{So,} \quad r_{Na^+}+r_{F^-}=2.31 \quad \ldots \quad \ldots \quad \ldots \quad (D)$$

Solving (C) and (D) we get

$$r_{Na^+}=0.95\text{Å} \text{ and } r_{F^-}=1.36\text{Å}$$

With our knowledge of these values for the radii of $Na^+$ and $F^-$ ions, the radii of other ions can be computed in the following manner. First of all, a compound of the same structure-type, containing either $Na^+$ or $F^-$, say, NaCl is chosen. In the next step, the internuclear distance $(r_{Na^+}+r_{Cl^-})$ is determined by X-ray deffraction technique and the known value $r_{Na^+}$ is deducted from the experimentally determined $(r_{Na^+}+r_{Cl^-})$ distance to arrive at the value of $r_{Cl^-}$. Similarly, the value of $K^+$ can be easily obtained by a similar procedure using KF as the test compound.

**Screening constant :** In a multi-electron atom, the force of attraction between the nucleus and the outer electron(s) is much diminished by the existence of other electrons in the underlying shells. This effect is known as **shielding effect** or **screening effcet.** Due to this, the nuclear charge ($Z$) of an atom is diminished by an amount S, which is called the **screening constant.** Screening constant is thus the measure of the degree to which the other electrons in the atom are able to shield or screen the nucleus from a given electron.

It has already been stated that the degree of penetration of electrons (of a given principal quantum number) into the charge cloud set up by the lower-lying electrons decreases in the order $s>p>d>f$. As a result of its greater extent of penetration, an *s* electron screens the nucleus more effectively than a *p* electron, and a *p* electron screens the nucleus more effectively than a *d* electron, and so on. Thus, the lower-lying $3s^2$ and $3p^6$ electrons in potassium (Gr IA) screen its nucleus more effectively than the $3d^{10}$ electrons can screen the nucleus of copper (Gr IB). So, the less penetrating *d* electrons cannot screen as effectively as the more penetrating *s* and *p* electrons.

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[1] See below for a detailed discussion on screening constant.

[2] See page 83 for Slater's rule and its applications.

To determine the **screening constant** for a particular electron, **the empirical rule of Slater** is generally used. For this purpose, the electrons are divided into a number of groups, and each electron of such a group is assigned to contribute its share to the screening effect. The sum total of all such contributions is the required screening constant. The assigned contributions are : (a) nothing for any electron which is farther from the nucleus than the given electron, (b) 0.35 for each additional electron which lie in the same shell as the given electron, (c) 0.85 for each electron in the next inner (lower-lying) shell, (d) 1.00 for each electron closer to the nucleus than those in (c), and (e) if the given electron is in a *d* or *f* sub-shell, an amount of 1.00 by each electron in a lower shell. Thus, the screening constant for an outermost electron of lead (atomic no.$=82$ and electronic configuration$=1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^2$) is, $0{\cdot}35\times4+0{\cdot}85\times18+1.00\times60=76{\cdot}7$, so that the effective nuclear charge ($Z_{eff}$) of Pb is $82-76{\cdot}7=5{\cdot}3$.

## Diagonal relationship.

We have noted that the atomic radii and hence the size of the atoms **increase** as we go down a group and that they **decrease** as we move across a period from left to right. Sometimes it so happens that these two effects almost counteract each other and in those cases we come across **diagonal relationship** in the periodic table. In such a case, the first element of a particular group (in the first short period) shows some chemical similarity with the second element of the next group (in the second short period). In figure 2.8 the elements showing diagonal relationship are connected by slanting arrows.

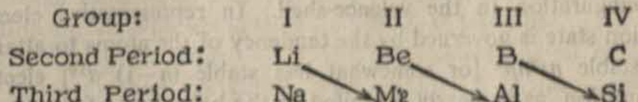


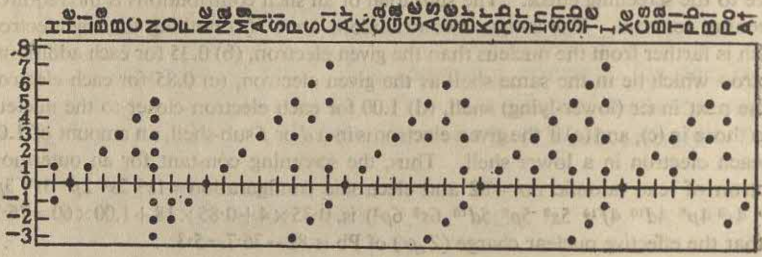
Fig. 2.8

Thus lithium, the first alkali metal of Gr. IA, shows some chemical similarity to magnesium, the second member of the next group IIA. Similarly, beryllium resembles aluminium and boron is somewhat similar to silicon.

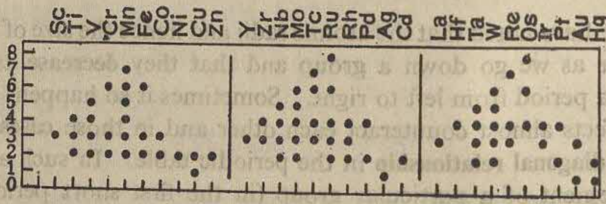
Many other properties of the elements and their compounds exhibit periodic change, which are the results of the periodic variation of one or more of the important fundamental characteristics discussed before. Some of them will be described now.

## 1. OXIDATION STATES.

Periodic regularities are observed in the occurrence of the oxidation states of the elements. The more important oxidation states of the elements are given in Fig. 2.9. If one can grasp the regularities of the occurrence of these oxidation states, it will help to remember some important chemistry of the elements.



*The representative elements*



*The transition elements*

Fig. 2.9

In most of the elements, oxidation states are related to the electronic configuration in the valence-shell. In representative elements, oxidation state is governed by the tendency of the atoms to attain the most stable $ns^2np^6$ [or somewhat less stable $(n-1)\ d^{10}$] electronic configuration, as is clearly exhibited in the behaviour of the elements of groups IA, IIA and the lighter members of IIIB. However, among the heavier members of IIIB, having $ns^2np^1$ configuration, the use of the $np^1$ electron gives rise to +1 oxidation state, in addition to the +3 oxidation state, corresponding to the use of all the three $ns^2np^1$ electrons. Thus, both indium and thallium shows +1 and +3 oxidation states. Such preferential removal of the $np$ electrons also occurs among the higher members of groups IVB, VB, VIB and VIIB. Thus, tin and lead in group IVB, having $ns^2np^2$ configuration, exhibit oxidation states of both +2 and +4. Arsenic and antimony of group VB, with $ns^2np^3$ configuration, also exhibit oxidation states of +3 and +5.

In the groups IIIB, IVB, VB, VIB and VIIB, where two different positive oxidation states are found to occur, the lower oxidation state, corresponding to the use of the $np$ electrons, becomes more and more important as one proceeds down the group. Thus, carbon and silicon (in Group IVB) exist exclusively in the +4 oxidation state, while for tin and especially lead, the stable oxidation state is +2. Similarly, +5 oxidation state in bismuth (Group VB), is extremely unstable. This is due to what is known as the **inert pair effect.** This happens because of the rather sharp increase in the size of the *ns*-orbitals with the increase in atomic number in a particular group, as a result of which the electron density in these *ns* orbitals decreases considerably. Hence, the bonds formed by the involvement of these *ns*-orbitals are rather unstable.

The negative oxidation states are most important in the case of non-metals and they appear from group IVB. Carbon exhibit negative oxidation states in many of the carbides and silicon does so in silicides and some other compounds. Nitrogen and phosphorus exist in the −3 oxidation state in nitrides and phosphides. But, in arsenic and antimony, the −3 oxidation state becomes very unstable and it is practically absent in bismuth. In group VIB, the −2 oxidation state is important for the lighter members, but not for the heavier ones. This is also true for the −1 oxidation state in Gr. VIIB elements. Thus, among the non-metals, the negative ion, corresponding to the gaining of electrons to attain the $ns^2np^6$ configuration becomes progressively unstable in a particular group with the increase in atomic number. This facile occurrence of the negative oxidation states among the lighter non-metals is consistent with their high electronegativity.

Though the transition elements exhibit a variety of oxidation states, some regularities and trends of variation are still observed. Transition metals with the *d*-level half-filled or less filled, *i.e.* having valence-shell configurations $(n-1)\ d^{1-5}\ ns^2$, exhibit highest oxidation states equal to their respective group numbers. Thus, scandium (IIIA), titanium (IVA), vanadium (VA), chromium (VIA) and manganese (VIIA) show maximum oxidation states of +3, +4, +5, +6 and +7 respectively. This is also true for the higher members of these groups, *i.e.*, for the corresponding members of the second and the third transition series. For those members of the first transition series, which have the outermost configuration $(n-1)d^{6-10}ns^2$, however, the oxidation states greater than +2 and +3 are less important Thus, +2 and +3 oxidation states dominate the chemistry of iron and cobalt, while the +2 state is of widest occurrence in the case of nickel, copper and zinc. The +8 oxidation state, corresponding to the removal of all the valence-electrons of iron, does not exist at all However, this +8 oxidation state is attainable, and is of considerable importance in ruthenium and osmium,—the higher congeners of iron.

It is to be noted here that, as the atomic number increases within a particular group of transition elements, the higher oxidation states become more important. Thus, the oxidation states of +2, +3 and

+6 are important in the chemistry of chromium, but in the case of molybdenum and tungsten, only the +6 oxidation state is of primary importance. It must be observed here that, this **progressive increase in the stability of the higher oxidation states** in a particular group of transition elements is just the opposite of what is found in the case of *representative elements*, due to the operation of the **inert pair effect** in the latter class.

**Chemical properties of the oxides.**

Oxides are binary compounds of oxygen with other elements in which oxygen occurs in an oxidation state of −2. Excepting fluorine (the only element which is more electronegative than oxygen), all other (representative, transition and inner transition) elements form oxides. The oxides of elements, well-removed in position from oxygen in the periodic table, are the stablest. Oxides can be classified into basic, amphoteric and acidic oxides. The basic oxides yield $OH^-$ ions on reaction with water, while the acidic oxides on reaction with water release protons in aqueous solution. Amphoteric oxides do not react with water, but dissolve in both strong acids and alkalis. Some acidic oxides do not dissolve in water, but dissolve in strong alkalis. Some basic oxides dissolve in acids, though they are insoluble in water. The elements on the left of the periodic table, *i.e.* the metals, form basic oxides. The basic character of the oxides decreases from left to right of the periodic table, but increases with atomic number in a

TABLE 2.18

| IA | IIA | IIIA | IVB | VB | VIB | VIIB |
|---|---|---|---|---|---|---|
| $Li_2O$ | $BeO$ | $B_2O_3$ | $CO_2$ | $N_2O_5$ | | |
| $Na_2O$ | $MgO$ | $Al_2O_3$ | $SiO_2$ | $P_4O_{10}$ | $SO_3$ | $Cl_2O_7$ |
| $K_2O$ | $CaO$ | $Ga_2O_3$ | $GeO_2$ | $As_2O_5$ | $SeO_3$ | $Br_2O_7$ |
| $Rb_2O$ | $SrO$ | $In_2O_3$ | $SnO_2$ | $Sb_2O_5$ | $TeO_3$ | $I_2O_5$ |
| $Cs_2O$ | $BaO$ | $Tl_2O_3$ | $PbO_2$ | $Bi_2O_5$ | | |

Basic character increases ↓

Ionic character increases ↓

Acidic character increases

⟶

Covalent character increases

particular group or family. Acidic oxides are formed by the non-metals which occupy the upper right hand side of the periodic table. Acid-base properties of some oxides of the representative elements are presented in Table 2.18.

Thus, among the *representative* elements, the oxides of metals are mostly basic and only a few are amphoteric. The oxides of metalloids are feebly acidic, while the oxides of non-metals are acidic.

Transition metals form different types of oxides in different oxidation states, and in general, the acidity of the oxides increases with the increasing oxidation number. Thus, CrO is basic, $Cr_2O_3$ is amphoteric, while $CrO_3$ is distinctly acidic.

**Properties of the hydrides.**

Binary compounds of hydrogen with other elements are called hydrides, and on the basis of physical and chemical properties, hydrides are classified as (i) saline hydrides (ii) interstitial hydrides and (iii) covalent hydrides. Hydrogen forms stable compounds with the elements of groups IA and IIA, in which it is present as the $H^-$ ion, and the compounds are ionic or salt-like in character. It also forms stable molecular hydrides with Gr. VB, VIB and VIIB elements, in which it is covalently bonded and such compounds are classed as covalent hydrides. The heavier elements of groups IIIB, and IVB and VB form very unstable hydrides, if combination takes place at all. B, C, Si and Ge form more than one hydrides, but only the simplest member is considered here. The next table (Table 2.19) shows the hydrides of representative elements along with the trends in some of their important characteristics.

Many of the transition metal hydrides are non-stoichiometric in character. The small hydrogen atoms occupy interstitial positions in the crystal lattice of the metals and hence they are also called *interstitial hydrides*. In several cases, such as those with palladium, platinum and nickel, which absorb varying quantities of hydrogen depending on the experimental conditions, it is difficult to conclude with certainty whether they are true compounds or not.

TABLE 2.19

| | | | | | | |
|---|---|---|---|---|---|---|
| LiH | $BeH_2$ | $B_2H_6$ | $CH_4$ | $NH_3$ | $H_2O$ | HF |
| NaH | $MgH_2$ | $AlH_3$ | $SiH_4$ | $PH_3$ | $H_2S$ | HCl |
| KH | $CaH_2$ | $Ga_2H_6$ | $GeH_4$ | $AsH_3$ | $H_2Se$ | HBr |
| RbH | $SrH_2$ | $InH_3$ | $SnH_4$ | $SbH_3$ | $H_2Te$ | HI |
| CsH | $BaH_2$ | $TlH_3$ | $PbH_4$ | $BiH_3$ | | |

From left to right :

(i) Covalent character increases.
(ii) Reducing character decreases.
(iii) Acidic character increases.
(iv) Thermal stability increases.
(v) Volatility increases.

From top to bottom :

(i) Ionic character increases.
(ii) Reducing character increases.
(iii) Basic character increases.
(iv) Thermal stability decreases.
(v) M.P. and B.P. increase.

We have by now discussed quite a number of more important general properties of the elements and some of their important compounds. We have tried to emphasise that, it is of great help to recognise how and why such properties of the elements like ionization energy (or ionization potential), atomic volume or radii, ionic radii, oxidation states, properties of oxides and hydrides are correlated with their electronic configurations. We have also discussed how these variations help us predict the similar properties of an element on the basis of the knowledge of its position in the periodic table which reflects the actual electronic configuration of the element in question.

CHAPTER III

# CHEMICAL BONDING AND THE STRUCTURE OF MOLECULES

A chemical bond may be defined as the force existing between two atoms or groups of atoms, holding them together to keep their independent existence as an aggregate or a molecule. Examples of the occurrence of chemical bonds pervade nature, and all the polyatomic species, elemental and compound, are examples of atoms bound together by chemical bonds.

The formation of a chemical bond between two or more reacting atoms must be associated with a lowering of energy, *i.e.* the energy-content of the products must be lower than the total energy of the reacting atoms. When the energy lowering in such a process exceeds 10 Kcals/mole as two atoms react, **a chemical bond** is said to be created between them. In fact, a chemical reaction between two molecules of reactants is a process of exchange of one bonding arrangement for another which has a lower energy and consequently is stabler. Thus, when a molecule of hydrogen and a molecule of chlorine react to form two molecules of hydrogen chloride, the bond between the two hydrogen atoms in the hydrogen molecule and that between the two atoms of the chlorine molecule are exchanged for the bond between the hydrogen and the chlorine in the two hydrogen chloride molecules.

## Why is the study of chemical bonding so important ?

From the above discussion it is clear that, the stabilisation of a product due to the formation of new chemical bonds between the components, leads to new chemical properties which are characteristic of that particular species. Thus, two different compounds can be represented by the molecular formula $C_2H_6O$. These are dimethyl ether ($CH_3.O.CH_3$) and ethyl alcohol ($CH_3CH_2OH$). These two compounds differ widely in physical and chemical properties due to different bonds existing between the atoms in their molecules. This shows clearly that the properties of molecules are almost entirely dependent on the actual structure, and not on the empirical composition. Thus, to have a proper insight of the chemical and physical properties of the elements and their compounds, a thorough understanding of the phenomenon of chemical bonding is absolutely essential.

It is clear from the above discussion that ionic compounds will be formed between elements belonging to groups widely separated from each other in the periodic table. The metallic elements in the extreme left side of the periodic table (IA and IIA), due to their low ionization potential and large atomic volume, easily form cations with the electronic configuration of the preceding intert gas. The non-metals of the right side of the periodic table (VIIB and VIB) form anions with ease, which have the electronic configuration of the next inert gas. Thus, the compounds of the alkali and the alkaline earth metals with the halogens and the chalcogens (Group VIB) are ionic in character. We can now conclude that the ease with which cations and anions are formed controls the formation of ionic compounds. The formation of cations and anions from atoms are dependent on the following factors :

(1) Ionization potential or ionization energy, (2) Electron affinity and electronegativity and (3) Lattice energy of the compound formed.

The effect of the first two factors on the formation of cations and anions respectively has been discussed in details in the chapter on the periodic classification of elements. So, it will be just mentioned here that low value of ionization potential favours the formation of cations and high electron affinity indicates pronounced tendency to form anions. The role of lattice energy will now be discussed in details.

**Lattice energy.**

The energy released when one formula-weight of an ionic crystal-lattice is formed by the regular arrangement of the requisite number of anions and cations in a definite pattern, is termed the **lattice energy.** Since an ion is considered as a hard sphere with the charge evenly distributed on its surface, the process of formation of an ionic compound AB, will not stop after the formation of the aggregate AB, because, the residual charges on the spherical $A^+$ and $B^-$ will attract similar ion-pairs. Such a process may be represented by Fig. 3.2.

As two ion-pairs approach each other, along with the attractive force between the cation and the anion, a repulsive force between ions bearing the same charge $B^-$, $B^-$ and $A^+$, $A^+$ will also come into play. But, in such an assembly, the distance $A^+ - A^+$ and $B^- - B^-$, measured from their centres (Fig 3.2) is larger than the $A^+ - B^-$ distance. Since the force of coulombic interaction varies inversely as the square of the distance between the centres of the charged spheres, the attractive force is much greater than the repulsive force. As a result, the potential energy decreases and the system becomes more stable. Thus, the stability of the system will increase progressively as more and more ion-pairs join the group, *i.e.* larger the crystal, lower will be the potential

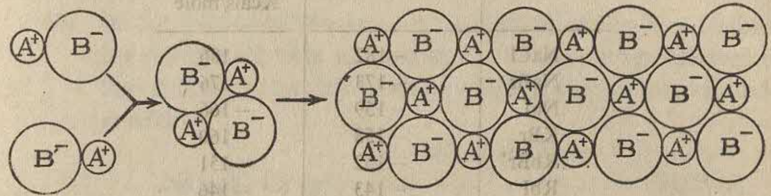

$A^+$
$B^-$
$B^-$
$A^+$
$B^-$
$A^+$
$A^+$
$B^-$
$A^+$ $B^-$ $A^+$ $B^-$ $A^+$ $B^-$ $A^+$ $B^-$
$B^-$ $A^+$ $B^-$ $A^+$ $B^-$ $A^+$ $B^-$ $A^+$
$A^+$ $B^-$ $A^+$ $B^-$ $A^+$ $B^-$ $A^+$ $B^-$

Fig. 3.2

Combination of two ion-pairs to form a small group and subsequent growth of a crystal.

energy of the system. The limit of the size of the crystal is set by several factors, of which the experimental conditions of crystal-growth is very important.

The value of lattice energy, U, can be calculated from the equation,

$$U = -\frac{Ae^2Z_+Z_-N}{r}\left(1-\frac{1}{n}\right), \quad \ldots \quad \ldots \quad (3.1)$$

where U=lattice energy ; $Z_+$ and $Z_-$=charges on the positive and the negative ions; $e$=electronic charge; N=Avogadro's number; $r$=inter-ionic distance in the crystal lattice ; A=Madelung constant, (It is the geometrical correction factor and its value depends on the type of the crystal lattice) ; $n$=a constant called the Born exponent. (This is associated with the repulsion between the ions and is often assumed to be equal to 9.)

Involvement of several variables in the above equation for the lattice energy indicates that its magnitude depends on various factors. Of all these factors, the oxidation state or the valency of the ions is of prime importance. The lattice energy will also increase if the radius of either the cation or the anion decreases. The theoretical values of the lattice energies of some alkali metal halides, along with the corresponding values obtained experimentally, are shown in the table 3.1.

TABLE 3.1

| Halides | Lattice energy calculated Kcals/mole | Lattice energy experimentally observed Kcals/mole |
|---|---|---|
| NaCl | −182 | −186 |
| NaBr | −173 | −176 |
| NaI | −159 | −166 |
| KBr | −158 | −160 |
| RbBr | −152 | −151 |
| RbI | −143 | −146 |
| CsI | −135 | −142 |

## FORMATION OF IONIC COMPOUNDS — ENERGY CONSIDERATIONS.

Let us now consider the formation of **one formula-weight** of sodium chloride from the elements, sodium and chlorine. Two different processes for its formation may be considered : (1) It can be done by the one-step direct reaction of the elements :

$$\mathrm{Na}\,(s)+\mathrm{Cl}(g) \longrightarrow \mathrm{NaCl}(s)\ -\mathrm{Q},$$
$$(\mathrm{Q}=98{\cdot}3\ \text{Kcals/mole}),$$

where Q=heat of formation of NaCl. The negative sign indicates that heat is evolved, *i.e.* the reaction is *exothermic* or *exoergic*.

(2) The formation of solid sodium chloride may also be visualised to take place through the following three steps :

(a) In this step, the sodium atom in the solid state is vaporized by supplying its sublimation energy (S), and the dissociation of the gaseous chlorine molecule to chlorine atoms is effected by supplying its dissociation energy **(D)** :

$$\mathrm{Na}\,(s) \xrightarrow{+\mathrm{S}\ (26{\cdot}0\ \text{Kcals/mole.})} \mathrm{Na}\,(g)$$
$$\tfrac{1}{2}\mathrm{Cl}_2(g) \xrightarrow[+\frac{1}{2}\,\mathrm{D}\ (28{\cdot}8\ \text{Kcals/mole})]{} \mathrm{Cl}(g)$$

(b) The second step is the conversion of the gaseous atoms into the respective ions,

$$\mathrm{Na}\,(g) \xrightarrow[+\mathrm{I}\ (119\ \text{Kcals/mole})]{+\text{Ionization energy}} \mathrm{Na}^+(g)$$

$$\mathrm{Cl}\,(g)\ \xrightarrow[-\text{E (86 Kcals/mole)}]{\text{Addition of } e^- \text{ (Electron affinity)}}\ \mathrm{Cl}^-\,(g).$$

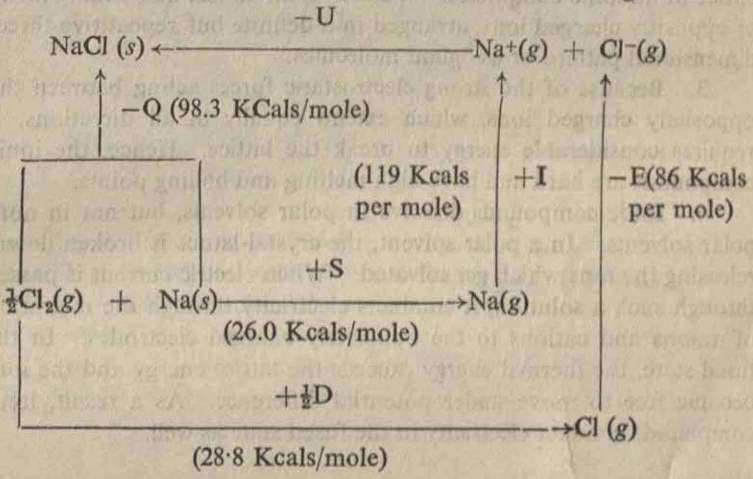
For the formation of $Na^+$, energy has to be supplied, while in the formation of $Cl^-$, energy is released.

(c) In the third step, the ions are brought close together to form the sodium chloride crystal-lattice, and the energy released in this process is the lattice-energy (U) of the sodium chloride crystal :

$$\mathrm{Na}^+(g)+\mathrm{Cl}^-(g)\ \xrightarrow[\text{Lattice formation}]{-\text{U(182 Kcals/mole)}}\ \mathrm{NaCl}\,(s)$$

This lattice energy, U, is a direct measure of the stability of the ionic crystal.

All the above processes can be combined together in a cyclic process, known as the **Born Haber cycle,** one form of which is given below:



Born Haber Cycle for the formation of one formula-weight of NaCl

According to Hess's **Law of constant heat summation,** the total energy-change in a process depends only on the energy of the initial and the final states of the reactants and the products, and not on the path followed. Thus, the heat of formation, Q, is equal to the sum of the quantities involved in the other way round the cycle,

$$-Q=+S+\tfrac{1}{2}D+I-E-U.$$

If all the other quantities are known, U can be easily calculated, and in this case, U is found to be 186·1 Kcals/formula-weight of NaCl.

The quantities Q, S, D and I can be experimentally determined, and the knowledge of E along with them, will lead to the evaluation of the lattice-energy, U, which is very difficult to obtain experimentally. The lattice-energy of an ionic crystal thus represents the stability of the crystal-lattice, and in order to break up the lattice and to force the constituent ions from their lattice positions far away from each other outside their own spheres of action, an energy equivalent to the lattice-energy must be spent. The energy required to break the ionic bonds present in one formula-weight of an ionic compound is called the **bond energy.** The bond energies of the chemical bonds lie in the range of 10 Kcals to 100 Kcals per mole.

## Properties of ionic compounds.

1. The building blocks or the chemical units of an ionic crystal-lattice are the oppositely charged ions, and not atoms or molecules.

2. No separate or discrete molecules are present in the crystal-lattice of an ionic compound. It exists as an almost non-ending array of oppositly charged ions, arranged in a definite but repeatitive three-dimensional pattern or as "giant molecules."

3. Because of the strong electrostatic forces acting between the oppositely charged ions, which extend equally in all directions, it requires considerable energy to break the lattice. Hence, the ionic compounds are hard and have high melting and boiling points.

4. Ionic compounds dissolve in polar solvents, but not in non-polar solvents. In a polar solvent, the crystal-lattice is broken down, releasing the ions which get solvated. When electric current is passed through such a solution, it conducts electricity through the migration of anions and cations to the oppositely charged electrodes. In the fused state, the thermal energy exceeds the lattice energy and the ions become free to move under potential difference. As a result, ionic compounds conduct electricity in the fused state as well.

## Solvation of ions and the role of solvation energy.

Ionic compounds dissolve in polar solvents. This happens because the polar solvent molecules exert attraction for the ions in the crystal-lattice of the solid solute, sufficient to pull them out from their respective positions. It is quite clear that, for an ionic compound to be soluble in a particular solvent, the system containing the ions dispersed in the solvent must be stable than the system of the ions present in the crystal lattice. Thus, there must be some type of interaction between the ions and the polar solvent molecules, leading to the release of some energy which helps to attain stabilisation. This happens in the following manner : When an ionic compound is put in a polar solvent, the negative ends of the solvent-dipoles attract the cations and the positive ends exert pull on the anions. The number of solvent molecules acting upon the ions depends mainly on the size of the ions and their charges. If this pull of the polar solvent molecules on the ions in the crystal-lattice exceeds the lattice energy of the solute, the lattice is broken down and the ions are dispersed within the solvent at distances far away from each other to have any appreciable attraction. The cations and the anions are surrounded by solvent molecules. This process of disruption of the crystal-lattice and dispersion of the ions from solid to the solution phase, encasing them with solvent molecules, is known as the process of **solvation of ions**. As a result of this solvation, an ion is stabilized as a separate solvated entity and an amount of energy, known as **solvation energy**, is released. **Whether an ionic solute will dissolve in a particular polar solvent will depend on the relative values of the lattice-energy and the solvation energy with respect to the solute-solvent pair.** If the solvation energy exceeds the lattice-energy, then the solute will go into solution. Like lattice-energy, it is difficult to obtain exact values of solvation energy. However, a Born-Haber type of cyclic approach yields useful relation between lattice energy, solvation energy and the heat of solution (see figure).

$$\begin{tikzcd}
MX(s) \arrow[rr, "+U"] \arrow[dr, "\pm L"'] & & M^+(g) + X^-(g) \arrow[dl, "-H"] \\
& M^+(\text{solv.}) + X^-(\text{solv.}) &
\end{tikzcd}$$

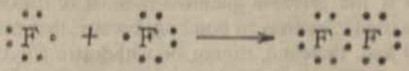
Here U is lattice energy, H is the solvation energy of the gaseous ion and L is the experimentally determined heat of solution at infinite dilution. Since the cycle is completed, the net energy-change will be zero, *i.e.* $\pm L + U - H = 0$, or $\pm L = U - H$.

The positive sign of L indicates heat absorbed and the negative sign denotes heat evolved. The Born equation, $H = \frac{e^2}{r}\left(1 - \frac{1}{\epsilon}\right)$, where $e$=charge on the ion, $r$=its radius and $\epsilon$=dielectric constant of the solvent, relates solvation energy (H) of an ion with the dielectric constant of the solvent in which the solution is being made. From the equation, it is clear that higher the value of the dielectric constant, greater is the solvation energy. Thus, for a particular solute, higher dielectric constant of a solvent indicates greater solubility of the solute in it. Both the lattice-energy and the solvation energy increase with decrease in anion and cation sizes. The lattice-energy increases more rapidly than the solvation energy when the charge on the cation or the anion is increased. The electronic arrangements of the cations in their valence-shell is also of importance, as the polarizing effects of the cation on the anions depend on the type of 'closed shell' of electrons in its valence-shell, the $d^{10}$–arrangement being more polarizing than the $s^2p^6$ configuration. The lattice-energy will increase more rapidly than the solvation energy, if the anion is polarized by the cation more readily than the solvent molecules, and as a result, solubility will decrease. Thus, we find that solubility of an ionic solute in a particular polar solvent is not an arbitrary phenomenon, but is regularly governed by certain specific properties of the solute-solvent pair. This explains the insolubility of $CaF_2$ in water, while all other halides, of calcium are soluble in water. The lattice-energy of $CaF_2$ exceeds the hydration energy of the $Ca^{++}$ and the two $F^-$ ions, while lattice-energy of $CaCl_2$, $CaBr_2$ and $CaI_2$ are less than the solvation energies of their constituent ions. A question may again arise as to why the lattice-energy of $CaF_2$ is greater than those of $CaCl_2$, $CaBr_2$ and $CaI_2$? The answer lies of the fact that, the radius-ratio of the cation and the anion, $r^+/r^-$, in $CaF_2$ is much higher than those in the other cases, and it is this ratio that primarily governs the magnitude of the lattice-energy through the value of Madelung constant.

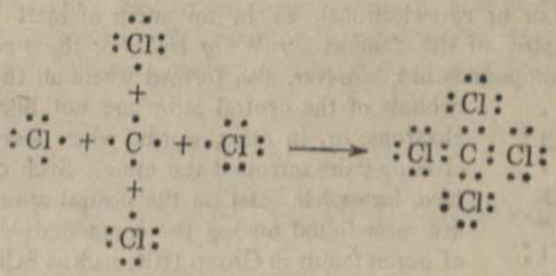
## THE COVALENT BOND.

That strong chemical bonds are present between atmos in homonuclear molecules like $H_2$, $O_2$, $N_2$ *etc.* are proved by the high energy required to dissociate them into their constituent atoms. Since both the atoms in all these molecules are identical in all their fundamental properties like ionization potential, electron affinity, electronegativity and electronic configuration in the valence-shell, electron-transfer from one atom to another is rather impossible, and hence the chemical bond between them cannot be of ionic type. We have already established that, the motive force behind the formation of a chemical bond is the inherent tendency of all atoms to attain the electronic configuration of the nearest inert gas in their valence-shells. Since it is not possible in the present cases to do so by mutual loss and gain of electrons, some other mechanism must be available for the attainment of the inert gas configuration. G. N. Lewis in 1916 was the first to point out that, **it is possible for atoms of comparable ionization potential and electronegativity to attain inert gas configuration by sharing one or more pairs of electrons.** Let us consider the formation of the fluorine molecule from two fluorine atoms. Fluorine is an element of Gr. VIIB of the periodic table and has an outermost electronic configuration of $2s^22p^5$.

Each fluorine atom contributes one electron to make a pair which is shared by both the atoms, and this may be represented diagramatically as :

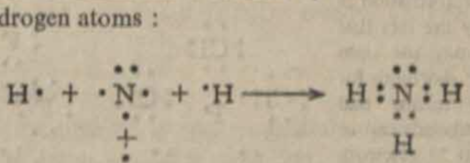


Thus, a pair of electrons (to which each fluorine atom contributes one electron) is shared between the two atoms so that each atom attains the stable octet, $2s^22p^5$-neon structure. In a similar manner, a molecule of $CCl_4$ is formed :



Carbon is an element of Gr. IVB of the periodic table, having $2s^22p^2$ electronic configuration, which is four short of the $2s^22p^6$-neon structure. So, it attaches with itself 4 chlorine atoms, forming four mutually shared electron-pair bonds, whereby both the carbon and the four chlorine atoms attain the stable octet structure.

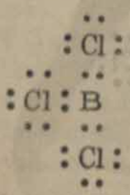
A molecule of ammonia is formed by the union of one nitrogen and three hydrogen atoms :



A hydrogen atom is one electron short of the helium configuration, while a nitrogen atom is three electrons short of neon structure. Thus, nitrogen attains of stable neon octet by forming three bonds with three hydrogen atoms, whereby the three hydrogen also attain helium structure. In this case, of the five electrons of the nitrogen atom, a pair of electrons (the $2s$ electrons) are not involved in bond formation with hydrogen. Such a pair of electrons, occupying a single orbital in the valence-shell of the central atom and not involved in bond formation (non-bonding) is called a **"Lone pair" of electrons.**

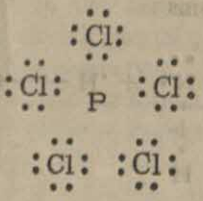
It may be remembered that the electrons that are involved in bond-formation are the highest energy electrons (*valence electrons*), *i.e. ns, np* and sometimes $(n-1)d$ electrons, where $n$ is the principal quantum number of the outermost shell. Core electrons cannot be used effectively in bonding, because they are bound too strongly to their own nuclei and, therefore, cannot be withdrawn effectively to the bonding region. They may contribute only slight repulsions in the overall bonding picture. Since the core electrons completely fill the inner orbitals, these orbitals are also eliminated from the consideration for bonding.

The covalent bonding, therefore, results from the sharing of electrons by two atoms till a maximum of eight electrons, or four pairs, surround each atom (except hydrogen, where it is one pair or two electrons), as in an atom of inert gas. This is the spirit of the famous *"rule of eight"* or the *"octet rule"*. Stable compounds are, however, also formed where all the available orbitals of the central atom are not filled up with electrons, or, in other words, where less than four electron-pairs surround the atom. Such compounds have **incomplete octet** on the central atom and they are most found among the compounds of elements of boron family in Group IIIB, such as $BCl_3$, $BF_3$ *etc.*, where the boron atom is surrounded by 6 electrons.

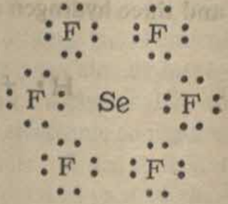


$BCl_3$

**Expansion of Octet.**—The octet rule strictly applies to those elements which has only four orbitals available (as in the elements of the two *short periods* of the periodic table). In these cases, a maximum of four covalent bonds can be formed. But, there are molecules where five or six covalent bonds are formed to a central atom. Such behaviour is exhibited by the elements of the *long periods* and the subsequent periods of the periodic table. Compounds like $PCl_5$, $SeF_6$ *etc.* are examples of this type. Their formation is accounted for by the fact that these elements may use upto two extra inner *d*-orbitals for bonding. This means that upto six covalent bonds can be formed and upto 12 electrons may surround these atoms in their compounds. This is why nitrogen and oxygen cannot form compounds $NCl_5$ or $OF_6$, as in these elements of the second period ($n$=2), there are no *d*-orbitals which may accommodate the extra electrons.



$PCl_5$

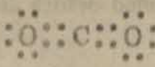


$SeF_6$

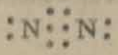
*The rule of two* : The examples cited above, along with many coordination compounds, metal carbonyls and nitrosyls, clearly indicate the lack of universal applicability of the rule of eight. So, instead of focussing so much attention on it, we should direct our attention to the more important and fundamental phenomenon of electron pairing. The recognition of the fact that the tendency of electrons to pair with each other is primarily responsible for a chemical bond formation is of prime importance and is almost universal in application. This tendency of two electrons to pair up and generate a stable electron-pair chemical bond is the spirit of *the rule of two* and is much more fundamental than the rather over-emphasised *rule of eight*.

### Multiple covalent bonds.

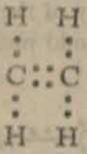
Just as a pair of electrons is shared between two atoms to form a covalent single bond, covalent multiple bonds, such as double bonds and triple bonds, can also be formed between two atoms by the mutual sharing of two and three electron-pairs respectively, each atom contributing one electron to each shared electron-pair. The structures of carbon dioxide, nitrogen molecule, ethylene and acetylene can be represented as :



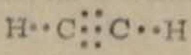
Carbon dioxide (2 carbon-oxygen double bonds)



nitrogen (1 nitrogen-nitrogen triple bond)



ethylene (1 carbon-carbon double bond)



acetylene (1 carbon-carbon triple bond)

A more meaningful treatment of multiple bonds has been given later under sigma (σ) and pi (π) bonds.

## ONE-ELECTRON AND THREE-ELECTRON BONDS AND ODD MOLECULES.

### One-electron bond.

The best example of a species containing **one-electron bond** is the hydrogen molecule-ion, $H_2^+$. The stability of this molecule-ion is due to the **resonance*** between the two equivalent electronic structures :

$$H\cdot H^+ \quad \text{and} \quad {}^+H\cdot H$$

The bond energy of this one-electron bonded species is 50 Kcals. per mole. The resonance interaction is large because the two structures are essentially identical.

---

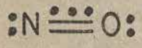
* A meaningful but brief discussion on resonance is given under "Formation of covalent bonds—energy consideration."

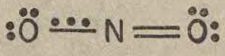
**Three-electron bond and odd molecules.**

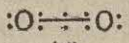
Odd molecules are molecules containing an odd number of electrons in them. They are few in number and are characterised by the presence of **three-electron bonds** in them. Some examples of such odd molecules, containing three-electron bonds, are NO, $NO_2$, $ClO_2$ and $O_2$ species. A three-electron bond between two atoms A and B may come into play as a result of resonance between the structures I and II :

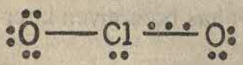
A : ·B and A· : B
I II

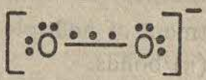
A resonance between I and II can occur to any significant extent, only if the two atoms have identical or nearly identical electronegativity. In fact, atoms differing by 0·5 units in electronegativity (Pauling's scale) in maximum, can form 3-electron bonds between them. A normal electron-pair covalent bond has a strength of twice that of a 3-electron bond. Generally, such odd molecules contain one or more normal electron-pair covalent bonds along with one 3-electron bond. This adds to the overall stability of the odd molecule as a whole. Electron dot structures of the four odd molecules mentioned before are given below :


(i)


(ii)


(v)

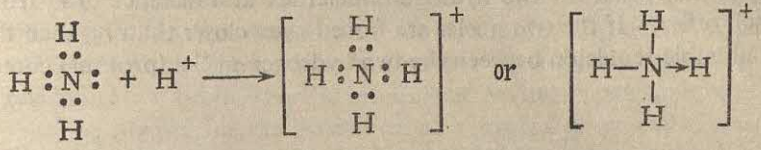

(iii)


(iv)

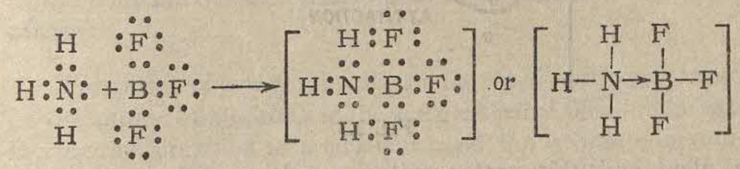
(i) Nitric oxide ;
(ii) Nitrogen dioxide ;
(iii) Chlorine dioxide ;
(iv) Superoxide ion ;
(v) Oxygen molecule.

## COORDINATE BOND.

A covalent bond results through the sharing of an electron-pair, each atom contributing one electron to the pair. Another type of shared electron-pair bond is also formed where both the electrons of the shared pair are contributed by only one of the reacting species. Thus, one atom acts as the **donor** (of the electron-pair), while the other acts as the **acceptor**. Such an electron-pair bond is called a *coordinate bond*, *coordinate covalent bond* or a *dative bond*, and is identical with the normal covalent bond except in the mode of its formation. Thus, ammonia molecule, which has one lone-pair of electrons, can react with a hydrogen ion, $H^+$, having the vacant *s*-orbital, by donating the lone-pair to the $H^+$, whereby the $H^+$ attains the helium duplet. Here, the $NH_3$ molecule, with one lone-pair, is called a "**donor**" and the $H^+$, which receives the lone-pair, is termed an **acceptor**.



Thus, a coordinate bond is formed by the **donor-acceptor interaction** of a species containing one or more lone-pairs of electrons and one which is **two** electrons short of an inert gas configuration, *i.e.* which possesses a vacant orbital to accommodate the lone-pair. Another example of coordinate bond formation is the reaction between ammonia and boron trifluoride :



Electron-pairs can also be donated into *d*-orbitals when such orbitals are available, as in the formation of $PF_6^-$(hexafluophosphate ion) and the most of transition metal complexes. In $PF_6^-$, the sixth bond is produced by using a lone electron-pair of $F^-$ ion and a *d*-orbital of phosphorus. In the $PF_6^-$ ion, one 4*s*, three 4*p* and two 3*d* (altogether six) orbitals available to phosphorus are used up.

The covalent bond is generally represented by a dash, while the coordinate bond is usually represented by an arrow.

**Formation of covalent bonds — energy considerations.**

We have already pointed out that the formation of a chemical bond takes place only if the mutual approach of the atoms is accompanied by a decrease in energy. Let us now consider the process of formation of a hydrogen molecule from two hydrogen atoms. When the hydrogen atoms are separated from each other by a large distance, there is no interaction between them and the potential energy of the system is conventionally taken as zero. As the two hydrogen atoms approach each other, potential energy gradually decreases as is shown in Fig. 3.3. The essential condition for such energy-lowering is that the two electrons belonging to the two hydrogen nuclei must have *opposite* or *anti-parallel spins.* The lowering of energy becomes maximum when the two hydrogen nuclei are at a distance of $r_0$ from each other. If the two nuclei are forced even closer than $r_0$, then the coulombic repulsion between the two hydrogen nuclei (protons) comes into play, and this proton-proton repulsion, being very strong, increases the energy of the system sharply and the system becomes highly unstable. Thus, when the two hydrogen nuclei are situated at a distance of $r_0$ from each other, the energy of the system is minimum. This state thus represents the hydrogen molecule, with $r_0$ being the length of the H—H bond.

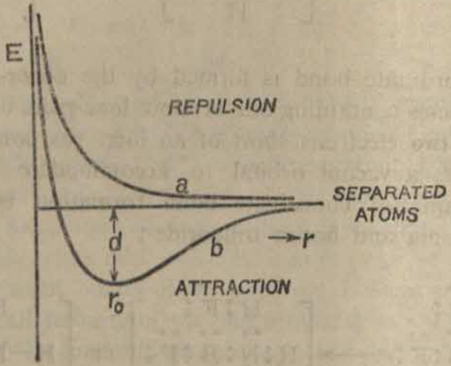


Fig. 3.3

The binding energy of such a homopolar or covalent linkage is derived from a **resonance** process between two states of equal energy. This principle of resonance is one of the most fundamental concepts of quantum mechanics and is applied in this case as follows : A system of two hydrogen atoms may be represented by two different states I and II of equal energy-content :

$$\underset{\text{I}}{\overset{\overset{1}{\cdot}}{H}_A \ \overset{\overset{2}{\cdot}}{H}_B} \quad \text{and} \quad \underset{\text{II}}{\overset{\overset{2}{\cdot}}{H}_A \ \overset{\overset{1}{\cdot}}{H}_B}$$

In state I, the electron denoted by 1 may be associated with the $H_A$ and the electron designated by 2 may belong to the nucleus $H_B$. In II, $H_A$ will occur with electron 2 and $H_B$ with electron 1. Since the two nuclei and the two electrons cannot be distinguished in reality when the two atoms approach each other, exchange of electrons between the two nuclei takes place with increasing frequency and becomes maximum when the two nuclei are at a distance of $r_0$ from each other. At this stage, neither of the two electrons may ultimately be regarded as belonging to any particular nucleus, but each will appear to belong to both. This results in the formation of the hydrogen molecule, in which the two hydrogen atoms are bonded by a pair of electrons localised mainly between the two nuclei. As only two electrons can reside in an '*s*' orbital (here 1*s* orbital) and as Pauli's exclusion principle must be obeyed for the formation of a hydrogen molecule, the two electrons belonging to the two atoms must have anti-parallel spins. Since a covalent bond is formed by the coupling of anti-parallel or opposite spins, the covalency exhibited by an element generally depends on the number of unpaired electrons present in the valence shell of the atom *at the moment* it is taking part in a chemical combination. This hypothesis of covalent chemical bonding through the coupling of unpaired spins of the valence-electrons was proposed in 1927 by Heitler and London and it also goes by the name, **the spin theory of valency.**

Formation of covalent bonds can also be visualised in terms of the participation of the orbitals in the valence-shell of the combining atoms. During the formation of a covalent bond, the orbital containing the unpaired electron of one atom approach a similar orbital of the other atom sufficiently closely, so that mutual overlap occurs and the shared electron-pair (with opposite spin) gets localised mainly in the region of overlap of the participating orbitals. Thus, the shape and orientation of the combining orbitals in space will determine the shape of the molecule formed.

## Structures of covalently bonded molecules.

As already pointed out in the formation of covalent bonds, the orbitals of the combining atoms containing single electrons, get occupied by electron-pairs. The constituent atoms of a covalently bound molecule, like the $NH_3$ molecule, contain three covalently bonded electron-pairs (bond-pairs) and one '*lone pair*' of electrons. Since electrons repell each other, the different orbitals containing electron-pairs will experience mutual repulsion and will thus tend to keep themselves away from each other as far as possible. In this way, they will experience minimum repulsion and hence attain maximum stability. This is the basic idea of the *Valency-Shell Electron-Pair Repulsion Theory* or the **VSEPR** theory proposed by Gillespie and Nyholm, which may be summed up as follows :

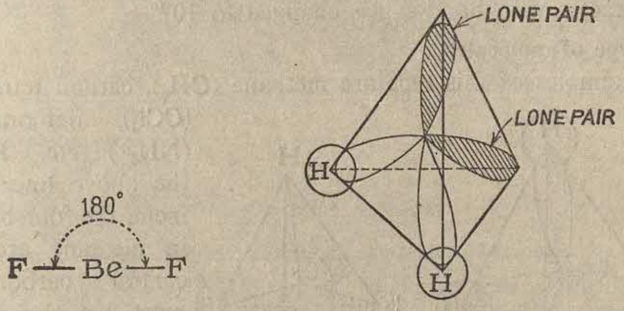
*For maximum stability of a molecule, the orbitals occupied by electrons in the valence-shell of the central atom should be so arranged in space that they lie as far away from each other as possible.*

The above statement is equally applicable to orbitals containing shared pair (bond-pair) of electrons as well as to those containing lone pairs (non-bonded pair) of electrons in the valence-shell. Thus, the geometry of a molecule depends on the spatial disposition of the orbitals with respect to each other around a central atom, *i.e.* on the angles which the orbitals in the valence-shell make with each other in space around the central atom. These inter-orbital angles are called **bond angles.**

Repulsion between different types of electron-pairs, according to the VSEPR theory, follow the trend : lone-pair : lone-pair > lone-pair : bond-pair > bond-pair : bond-pair. In the light of the VSEPR theory, we will now consider the shapes of the molecules of the types $AX_2$, $AX_3$ and $AX_4$. As the AX-type of molecules can have a linear structure only, it will need no discussion.

### $AX_2$-type of molecules.

By simple geometrical considerations, it can be shown that, if only two orbitals (or two electron-pairs) are present around the central atom A, the only possible way to keep them farthest apart is to keep them at an angle of 180° to each other. Thus, the $BeF_2$ molecule is linear with the F—Be—F bond angle 180° (Fig. 3.4). Here, the central atom beryllium has two bond-pairs in its valence-shell. Another type of $AX_2$ class of molecules is represented by water. In water, there are four pairs of electrons around oxygen, of which two are bond-pairs and two lone pairs, and hence are not equivalent. These four pairs of electrons will be placed at the four corners of a tetrahedron for minimizing repulsion. Since all these electron-pairs are not equivalent, the tetrahedron will be distorted and the H—O—H bond angles will deviate from the regular tetrahedral value of 109·5° and become 104°. This happens because the lone pair-bond pair repulsion is greater than the bond pair-bond pair repulsion, as a result of which the two lone pairs move apart and make the H—O—H angle smaller.



The beryllium fluoride molecule The water molecule

Fig. 3.4

**$AX_3$-type of molecules.**

If there are three orbitals (three electron-pairs) around the central atom A, in a molecule $AX_3$, the only way to keep them farthest apart is to make the X—A—X bond angle 120°. The molecule in such a case will be a plane equilateral triangle. Familiar examples are $BF_3$ and $BCl_3$ (Fig. 3.5).

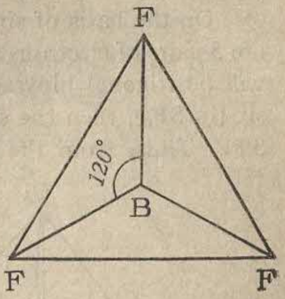


Fig. 3.5 ($BF_3$)

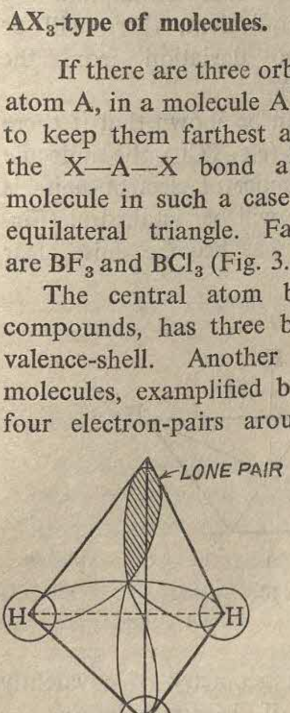


Fig. 3.6

The central atom boron, in these compounds, has three bond-pairs in its valence-shell. Another type of $AX_3$ molecules, examplified by ammonia, has four electron-pairs around the central element nitrogen, of which three are bond-pairs and one is a lone-pair. The only way to keep them farthest apart is to place them at the corners of a tetrahedron. However, in ammonia, all the electron-pairs are not equivalent. The three bonded electron-pairs are directed to three corners of a tetrahedron around nitrogen with the fourth lone-pair placed at the fourth corner as shown in figure 3.6. Due to greater repulsion between the lone-pair and the bond-pairs, the bond-pairs representing the N—H bonds will be repelled, and the H—N—H bond-angle will decrease to certain extent. Hence, the geometry of the $NH_3$ molecule will deviate from the regular tetrahedron and become pyramidal in character with bond-angles changed to 107°.

**$AX_4$-type of molecules.**

Examples of this type are methane ($CH_4$), carbon tetrachloride ($CCl_4$), ammonium ion ($NH_4^+$) *etc.* Following the above line of argument, the four bond-pairs in methane around the central carbon atom must be placed at the four corners of a regular tetrahedron. Since all the four bond-pairs are equivalent, there will be no deviation from the regular tetrahedral angles, of 109°28′ (Fig. 3.7).

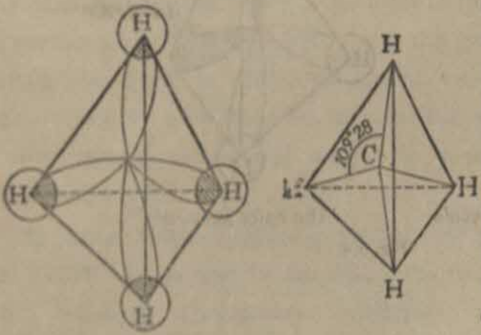


Fig. 3.7

On the basis of similar arguments, it can be shown that if there are 5 pairs of electrons around a central atom (*e.g.* $PCl_5$), the molecule will be trigonal bipyramidal, and if the number of electron-pairs is six (in $SF_6$), then the shape of the molecule will be octahedral (Fig. 3.8). Thus, from the above discussion, it has become quite clear that, according to the VSEPR theory, the geometry of covalently bonded molecules depends on the number of electron-pairs in the valence-shell of the central atom, and any distortion from the regular geometry is a consequence of the non-equivalence of the electron-pairs in the valence-shell.

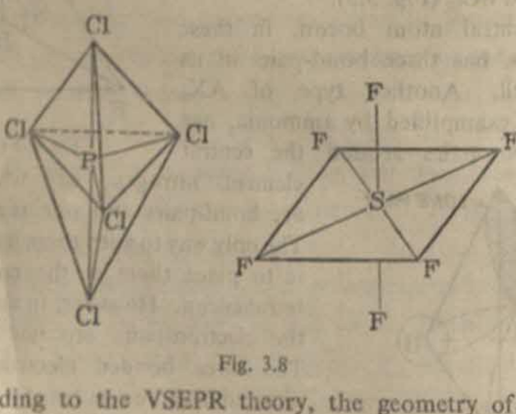


Fig. 3.8

It will not be out of place to mention here that, covalently bonded molecules can be structurally classified depending on the number of electron-pairs in the valence-shell of the central element. This classification is more convenient than the one depending on the molecular formula which is discussed above. Table 3.2 contains the molecular shapes dependent on the number of electron-pairs in the valence-shell.

### Some important properties of covalent compounds.

1. As the covalent compounds are formed by mutual sharing of electrons between atoms of comparable electronegativity, they do not ionize. Thus, they do not conduct electricity either in solution or in the fused state.

2. Most of the covalent compounds exist as discrete molecules in the liquid or in the solid state. In covalent solids, the force between the structural units are of weak Van der Waals type, and hence most of the covalent compounds are comparatively soft and have low melting and boiling points.

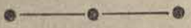
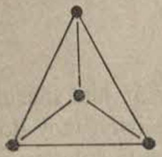
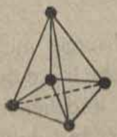
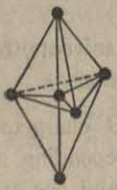
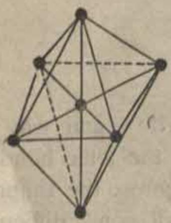
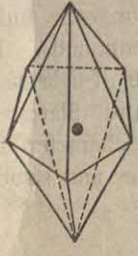
3. These compounds are soluble in non-polar solvents, but are generally not much soluble in polar solvents like water.

4. The covalent bond has definite directional character and such molecules have definite shape and structure, depending on the electronic configurations of the constituent atoms and the type of the bonds involved.

### Hybridisation.

At this stage of our knowledge, we know how and why the covalent bonding occurs and how it differs from the ionic bonding. From principles of the VSEPR theory, we can guess the shape of covalently bonded molecules. But, there are still some difficulties in correlating the **ground-state electronic configuration** of elements like beryllium, boron, carbon, phosphorus, sulphur *etc.* and the maximum covalency exhibited by them in their compounds. These difficulties can be overcome by invoking the principle of **hybridisation of electron-orbitals** as proposed by Pauling and Slater. The hybridisation principle also explains the directional character of the hybrid bonds in space, and takes care of the shapes and structures of covalently bonded molecules and ions.

TABLE 3.2

| Molecular shape | Electron pairs in valence-shell | Examples |
|---|---|---|
|  | 2 | Beryllium chloride, $BeCl_2$. |
|  | 3 | Boron trichloride. $BCl_3$.<br>Boron trifluoride, $BF_3$ |
|  | 4 | Methane, $CH_4$.<br>Silicon tetrachloride, $SiCl_4$ |
|  | 5 | Phosphorus pentachloride, $PCl_5$.<br>Phosphorus pentabromide, $PBr_5$. |
|  | 6 | Sulphur hexafluoride, $SF_6$<br>Selenium hexafluoride, $SeF_6$ |
|  | 7 | Niobium heptafluoride, $NbF_7$.<br>Tantalum heptafluoride, $TaF_7$. |

**Unpairing of paired electrons, promotion to higher-energy obitals and subsequent hybridisation of the singly occupied orbitals.**

*Formation of the $BeF_2$ molecule and explanation of its structure :*

We know that beryllium and fluorine react to form beryllium fluoride, represented as $BeF_2$. The electronic configuration of fluorine (at. no. 9) in the ground-state is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$. Since it has one unpaired electron in the $2p_z$ orbital, which can accommodate two electrons, it can form one covalent bond by utilising this half-filled $2p_z$ orbital by overlapping with another half-filled orbital of the beryllium atom. Now, the electron-configuration of the beryllium (at. no. 4) in the ground-state is $1s^2 2s^2$. Since it does not posses any orbital occupied by a single electron, it should not be able to form any covalent bond. How, then, is the $BeF_2$ molecule formed ? The answer is as follows : we have already pointed out that the formation of a chemical bond, whether ionic or covalent, takes place with the release of energy. Thus, when the beryllium atom and the two fluorine atoms are brought together in the range of the bonding distance, energy is released and this energy is utilised in unpairing the two 2*s* electrons of Be and promoting one of them to one of the 2*p* orbitals, say $2p_x$. Now, the activated or excited beryllium atom has two half-filled orbitals which it can use for bond formation. But, the bonds so formed will be different from each other, as one of them will use the 2*s* orbital and the other the 2*p* orbital. But, we know that the two Be—F bonds in $BeF_2$ are exactly identical, and the F—Be—F angle is 180°. These experimental facts can be explained by postulating that, the 2*s* and $2p_x$ orbitals in the activated beryllium atom interact with each other, resulting in the formation of two orbitals of equal energy which are identical in all respects. This process of redistribution of electrons in defferent orbitals in the valency-shell of an atom, creating a new set of identical orbitals, is known as **hybridisation**. The new orbitals are known as **hybrid orbitals**. Because of the involvement of one *s*- and one *p*-orbitals in the process of hybridisation here, this process is called **sp-hybridisation** and the bonds formed thereby are termed as the *sp*-hybrid bonds. The whole process is schematically represented in Fig. 3.9 :

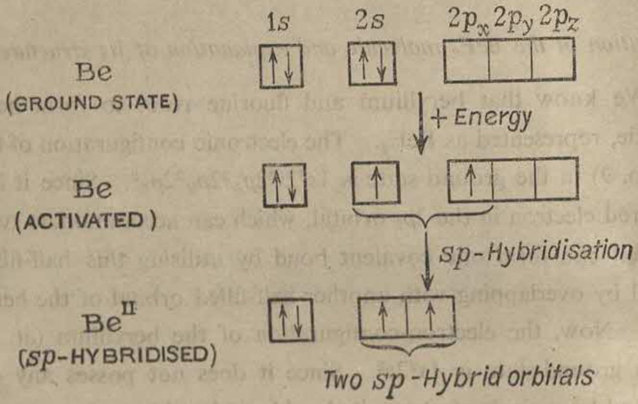


Fig. 3.9

**N.B.** It must be clearly understood that the pictorial representation of *sp*-hybridisation presented in figure 3.9 is just a conceptual model and is a rather over-simplified one. The ultimate process of hybridisation passes through the activated state, but the activated state can never be physically detected. So, the student must not think that the activated state has a physical existence like those of the ground state and the hybridised state. This is true for all types of hybridisation.

This *sp*-hybridisation can be pictorially represented by utilising the shape of the combining orbitals in the following manner :

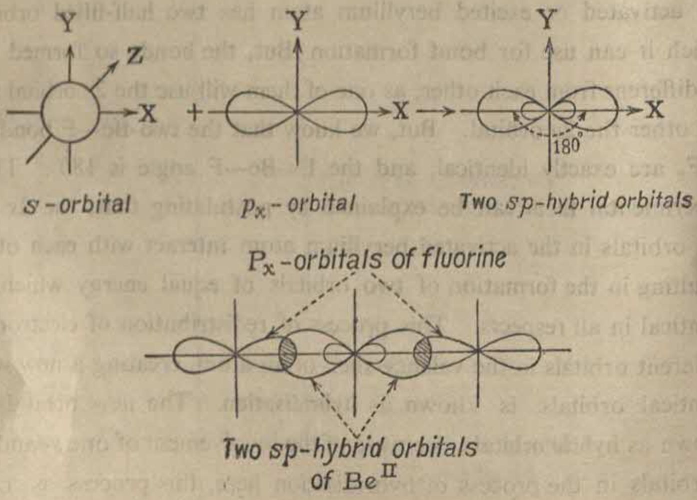


Fig. 3.10

The two *sp*-hybrid orbitals consist of one large lobe and one small lobe. During bond-formation, when these bigger lobes overlap with the $2p_z$ orbitals of the two fluorine atoms, strong covalent bonds are formed with the F – Be – F angle of 180°, as shown in the figure 3.10.

These hybrid bonds are stabler than those formed by either of the constituent orbitals. Just like the *sp*-hybridisation, forming two equivalent orbitals inclined at an angle of 180° with each other, different types of hybrid orbitals can be formed by the involvement of different numbers of *s*- and *p*-orbitals and also of *s*-, *p*- and *d*-orbitals, giving rise to a number of equivalent hybrid orbitals. The relative strengths of these hybrid bonds and their disposition in space round the central atom can be calculated by quantum-mechanical methods. Table 3.3 shows the relative strengths of such hybrid bonds, the inter-valence angles and the distribution of the hybrid bonds in space around the atom whose orbitals are hybridised.

TABLE 3.3

| Atomic orbitals involved in hybridisation | Hybridisation types | Shape | Strength of hybrid bonds (relative to the strength of an $s-s$ bond strength $=1$), and the inter-valency angle | |
|---|---|---|---|---|
| One *s* and one *p* | $sp$ | Linear | 1·93 | 180° |
| One *s* and two *p* | $sp^2$ | Plane triangle | 1·99 | 120° |
| One *s* and three *p* | $sp^3$ | Tetrahedron | 2·0 | 109°28′ |
| One *s*, three *p* and one *d* | $sp^3d$ or $dsp^3$ | Trigonal bipyramid | — | 120° and 90° |
| One *s*, three *p* and two *d* | $sp^3d^2$ or $d^2sp^3$ | Octahedron | 2·92 | 90° |
| One *s*, two *p* and and one *d* | $dsp^2$ | Square plane | 2·69 | 90° |

**$sp^2$-hybridisation.**

Boron, which has the ground-state electronic configuration of $1s^2 2s^2 2p^1$, forms boron trifluoride, in which the three B—F bonds are equivalent and directed towards the corners of an equilateral triangle, with the F—B—F angle of 120°. This happens due to the formation of three $sp^2$-hybrid orbitals which may be pictured as in fig. 3.11.

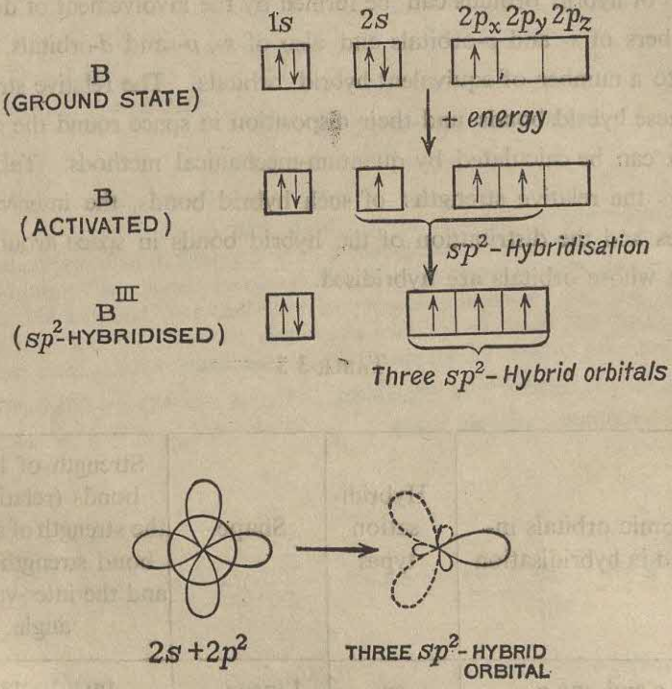


Fig. 3.11

These three $sp^2$-hybrid orbitals now overlap with the three $2p$ orbitals of the three fluorine atoms, forming the $BF_3$ molecule.

**$sp^3$-hybridisation.**

Carbon, with the ground-state electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1$, forms four equivalent bonds directed towards the corners of a regular tetrahedron, with the inter-valence angles of 109°28′, by undergoing $sp^3$-hybridisation as shown in fig. 3.12.

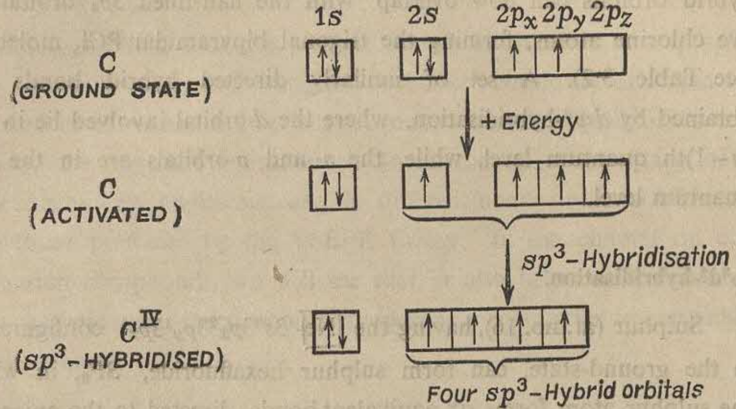


Fig. 3.12

These four $sp^3$-hybrid orbitals can now overlap with the half-filled (singly occupied) orbitals of other atoms like hydrogen, chlorine *etc.*, forming $CH_4$ and $CCl_4$ respectively.

**sp³d-hybridisation.**

Phosphorus (at. no. 15), with the ground-state configuration of $\boxed{\text{Ne}}$ $3s^2 3p_x^1 3p_y^1 3p_z^1$, forms $PCl_5$, in which phosphorus forms five

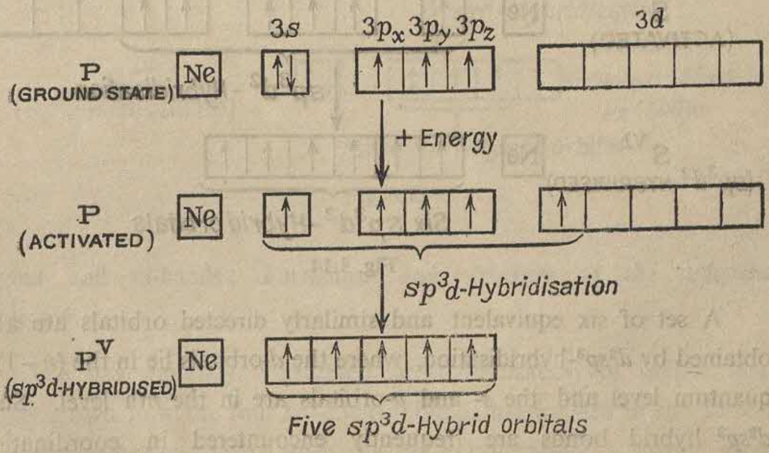


Fig. 3.13

bonds directed in space to the five corners of a trigonal bipyramid, due to the involvement of $sp^3d$-hybridisation. These five $sp^3d$ hybrid orbitals can now overlap with the half-filled $3p_z$ orbitals of five chlorine atoms, forming the trigonal bipyramidal $PCl_5$ molecule. (see Table 3·2). A set of similarly directed hybrid bonds are obtained by $dsp^3$-hybridisation, where the *d*-orbital involved lie in the $(n-1)$th quantum level, while the *s*- and *p*-orbitals are in the *n*th quantum level.

### $sp^3d^2$-hybridisation.

Sulphur (at. no. 16), having the [Ne] $3s^2 3p_x^2 3p_y^1 3p_z^1$ configuration in the ground-state, can form sulphur hexafluoride, $SF_6$, in which the sulphur atom forms six equivalent bonds, directed to the apices of an octahedron, by invoking $sp^3d^2$-hybridisation (fig. 3.14 and Table 3·2).

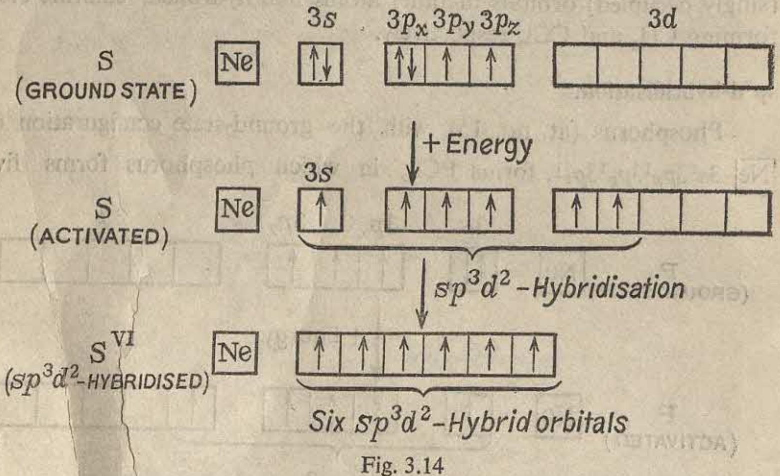

3s
3p<sub>x</sub> 3p<sub>y</sub> 3p<sub>z</sub>
3d
S (GROUND STATE)
Ne
+ Energy
3s
S (ACTIVATED)
Ne
sp³d² - Hybridisation
S<sup>VI</sup> (sp³d²-HYBRIDISED)
Ne
Six sp³d² - Hybrid orbitals

Fig. 3.14

A set of six equivalent and similarly directed orbitals are also obtained by $d^2sp^3$-hybridisation, where the *d*-orbitals lie in the $(n-1)$th quantum level and the *s*- and *p*-orbitals are in the *n*th level. Such $d^2sp^3$ hybrid bonds are frequently encountered in coordination complexes of transition metal ions and will be discussed in details in the chapter on coordination complexes. There we will come across the *dsp*²-hybridisation of orbitals, leading to complex formation.

Thus, we find that the process of hybridisation is conceptually very helpful to us in explaining the maximum covalency exhibited by the various elements, and helps us to understand the shape and structure of the covalent compounds. In all the cases, the shape of a molecule and the angles between the different bonds are in conformity with those predicted by the VSEPR theory. In the chapter on co-ordination compounds, we will see that, it also helps us understand the magnetic and spectroscopic properties of complex compounds in many cases.

**$sp^2$-hybridisation :**

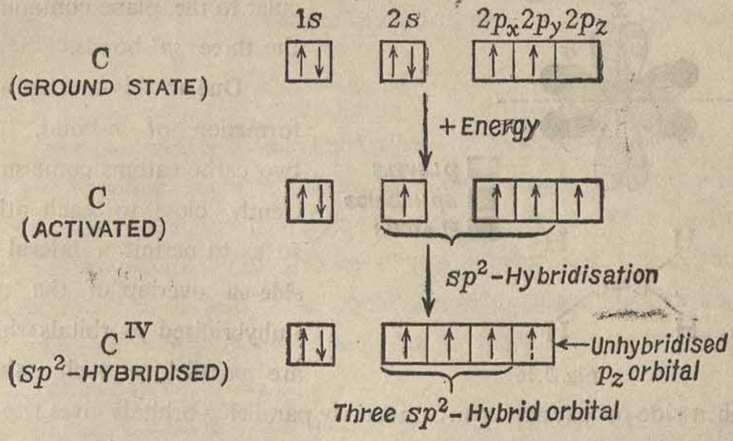


Fig. 3.15

**Sigma and pi-bonds : Formation and structure of the ethylene molecule.**

We have already considered *sp*³-hybridisation of carbon and have shown how the four *sp*³-hybrid bonds are utilised in the formation of methane. Apart from the *sp*³-hybridisation, a carbon atom can also undergo *sp*²-hybridisation as shown in the fig. 3.15.

When two such $sp^2$-hybridised carbon atoms combine, the first step is an overlap of two $sp^2$-hybrids (one from each of the carbon atoms) along their axes to give a σ-bond (sigma bond) as shown in Fig. 3.16 (first two pictures).

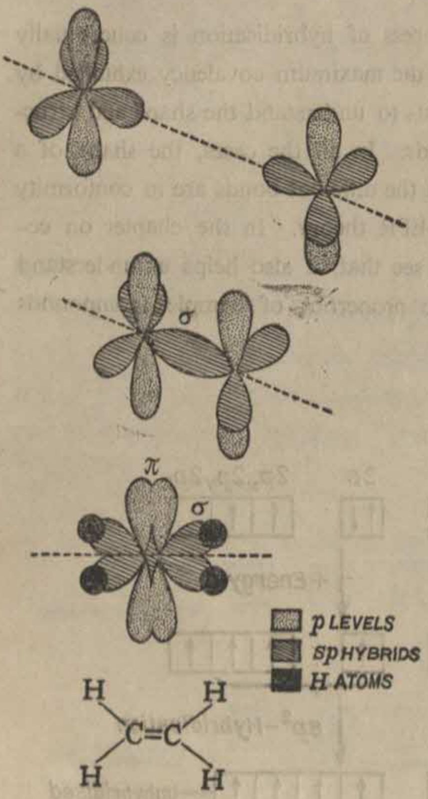


Fig. 3.16

From the case of boron, discussed before, we know that the three $sp^2$-hybrid bonds are arranged in one plane and are at 120° to each other. The remaining unhybridised $2p_z$ orbital of the $sp^2$-carbon is perpendicular to the plane containing the three $sp^2$-bonds.

Due to this overlap and formation of σ-bond, the two carbon atoms come sufficiently close to each other so as to permit a **lateral** or **side-on** overlap of the two unhybridised *p*-orbitals which are parallel to each other. Such a side-on overlap of two mutually parallel *p*-orbitals gives rise to **a π-bond.** It is quite obvious from the figure that, in this case, the overlapping regions of the *p*-orbitals are rather small, and hence π-bonds are weaker than σ-bonds. In general the energy of a carbon-carbon σ-bond is about 80 Kcals/mole, while that of a carbon-carbon π-bond is around 60 Kcals/mole. The figure also shows that carbon-carbon π-bonds are of shorter length (1.34Å) than the σ-bonds (1·54Å).

**Formation and structure of the acetylene molecule.**

Carbon atom can also undergo *sp*-hybridisation, leaving two of its *p*-orbitals in the unhybridised state. This may be represented as in fig. 3.17 :

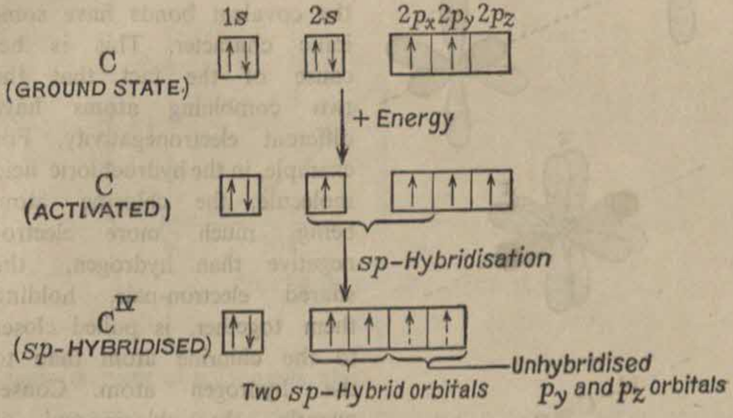
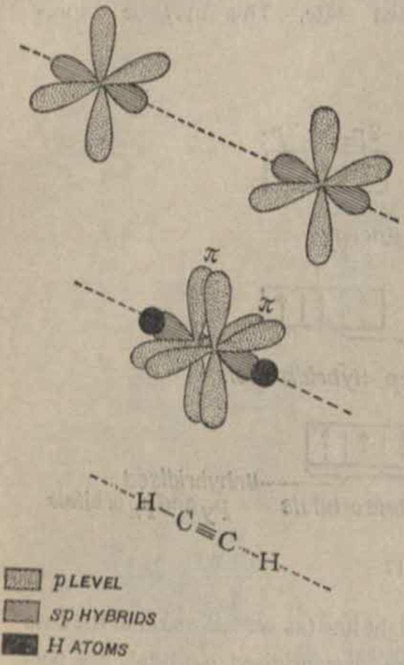


Fig. 3.17

The two *sp*-hybrids are in a straight line (as we have seen in the case of the beryllium atom) and both the unhybridised *p*-orbitals are perpendicular to the plane containing the two *sp*-hybrids. With the formation of the σ-bond by the overlap of two *sp*-hybrid orbitals of the two carbon atoms, the two nuclei come sufficiently close together and the two pairs of *p*-orbitals undergo side-on overlap, forming two π-bonds as is shown in fig. 3.18.

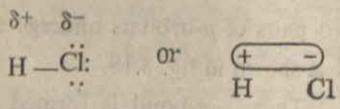
Thus, a σ-bond is formed as a result of overlap of the two *sp*-hybrid orbitals of the two carbon atoms along the axes of both the orbitals and a π-bond is formed by the lateral overlap of two **unhybridised** *p*-orbitals (or *d*-orbitals in the case of transition metals and heavier representative elements) lying parallel to each other. A carbon-carbon double bond is thus made up of one σ-and one π-bond, and a triple bond is composed of one σ- and two π-bonds. In general, we may note that, any multiple bond is a combination of σ- and π- bonds.

**Partial ionic character of covalent bonds.**



Fig, 3.18

It has been pointed out at the beginning of this chapter that, purely ionic and purely covalent bonds are of limited occurrence. Excepting the homonuclear covalent molecules, majority of the covalent bonds have some ionic character. This is because of the fact that the two combining atoms have different electronegativity. For example, in the hydrochloric acid molecule, the chlorine atom being much more electronegative than hydrogen, the shared electron-pair, holding them together, is pulled closer to the chlorine atom than to the hydrogen atom. Consequently, the chlorine-end of the molecule has some excess of negative charge located on it, while the hydrogen-end naturally assumes the complementary positive charge, leading to the formation of a permanent dipole. Such a molecule may be considered as two oppositely charged poles separated by the covalent bond. The greater the difference of electronegativity of the constituent atoms, the greater is the polarity of the bond. Thus, the H—F molecule is more polar than the H—Cl molecule. Based on the ionic characters of HI (4% ionic), HBr (11% ionic), HCl (19% ionic) and HF (45% ionic), Pauling graphically represented the variaton in the ionic character of a covalent bond as a function of the difference in electronegativity of the combining atoms (fig. 3.19).



From the graph, it is clear that 50% ionic character appears when the electronegativity difference is nearly 1·7. Thus, a difference in electronegativity larger than 1·7 indicates that the bond is more ionic than covalent, while a difference of less than 1.7 indicates predominantly covalent character.

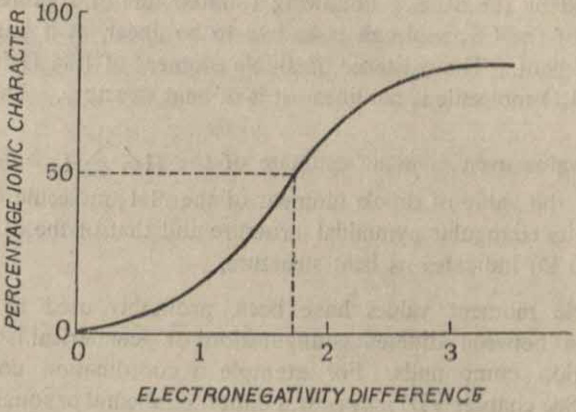
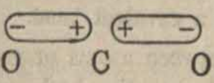


Fig. 3.19

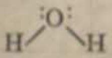
**Dipole moment of polar molecules.**

The extent of polarity of a molecule is expressed in terms of dipole moment ($\mu$) which is given by the product of one of the charges on the two ends of the dipole and the distance separating them, *i.e.* $\mu = e \times d$, where $e$=the charge at one end of the dipole and $d$=the length of the bond between the two atoms. The magnitude of the electronic charge is of the order of $10^{-10}$ esu and bond-lengths are of an order of $10^{-8}$ cms. Thus, the values of the dipole moments are of the order of $10^{-18}$, which is termed a **Debye** and is denoted by **D.** The dipole moment of the HCl molecule is $1{\cdot}03 \times 10^{-18}$ or 1·03 D.

A knowledge of dipole moment of a molecule sometimes yields valuable information about its structure. The dipole moment of a polyatomic molecule is obtained by the vectorial addition of the moments of the individual bonds constituting the molecule in question. The dipole moment of the $CO_2$ molecule is found to be zero. But, oxygen being more electronegative than carbon, the carbon-oxygen bond must have a polar character, with the oxygen-ends negatively and the carbon-end positively charged. But, there are two such dipolar entities in the $CO_2$ molecule as indicated below :



or $\overset{\delta-}{O}=\overset{2\delta+}{C}=\overset{\delta-}{O}$

Since it has a zero dipole moment, the $CO_2$ molecule must have a linear structure, in which the dipole moment of one half of the molecule is cancelled by the other. Following a similar line of arguments, the structure of the $CS_2$ molecule is known to be linear, as it has a zero dipole moment. The existence of dipole moment of 1.84 D indicates that the $H_2O$ molecule is not linear, it is of bent structure. The dipole moment value even gives an estimate of the  bond-angle. Similarly, the value of dipole moment of the $NH_3$ molecule (1.46 D) indicates its triangular pyramidal structure and that of the $SO_2$ molecule (1.60 D) indicates its bent structure.

Dipole moment values have been profitably used in making distinction between different configurations or geometrical isomers of coordination compounds. For example a coordination compound $MA_2B_2$ (See chapter VII) may posses either tetrahedral or square planar configuration. Two isomers of this complex, (**cis** and **trans**) are possible if it exists in the square planar configuration and the moments of the *trans*-planar isomer will be zero while that of the *cis*-planar arrangement will be quite large. A tetrahedral configuration should have a much lower dipole moment than that of the *trans* square planar isomer. $[Pt(NH_3)_2Cl_2]$ has two isomers, one with zero dipole moment which must be the *trans* planar isomer, while the other with a fairly high dipole moment value must be the *cis* isomer (see chapter VII).

## Some important aspects of the covalent bond in connection with organic reactions.

It is really superfluous to mention that the covalent bond almost completely dominates the realm of organic chemistry. Thus, any discussion on covalent bonding will be far from complete without the inclusion of some of the most important and fundamental principles which guide the reactions and properties of covalent organic molecules. The ways in which a covalent bond may first break and then undergo remaking in a different manner, resulting in newer products, and the reasons of such bond-breaking and re-making, should be understood in a general way. The following discussion is aimed at that direction in as brief a manner as possible.

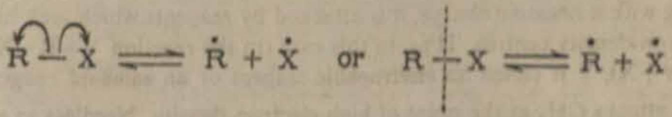
## Homolytic and heterolytic fission of a covalent bond.

In a chemical change, bonds between atoms or groups of atoms are broken first and then formed, or the both processes occur simultaneously. In order to classify the reactions of a **covalent compound,** let us consider the general reaction,

$$Y + R-X \longrightarrow R-Y + X \quad .. \quad .. \quad (5.1),$$

where both R – X and R – Y are covalent molecules. It is quite evident that, at first the electron-pair bond in R – X is broken and the bond R – Y is formed thereafter. There are two different ways in which the bond R – X can be broken.

(i) The electron-pair of the bond is equally shared by R and X, *i.e.* both R and X retain one electron out of the shared pair. This may be represented as :



Such a process of symmetrical bond-breaking, which is an **electron unparing** process, is called **homolysis** or **homolytic fission.**

Such a homolytic fission of a covalent bond gives rise to products each of which contains an unpaired electron and are known as **free radicals.** Reactions which involve the participation of such free radicals are termed **free radical reactions.** Examples of free radicals are alkyl radicals like methyl radical ( $\dot{C}H_3$), triphenyl methyl radical $(C_6H_5)_3\dot{C}$ *etc.*

Most of the free radicals contain an odd number of electrons (of which one is unpaired) and they are electrically neutral. But, a few free radical-ions are also known. Some free radicals contain two unpaired electrons (each resulting out of homolysis of one electron-pair bond), and are called **diradicals.** The most familiar example of a diradical is the methylene radical $:CH_2$, which is generally known as **carbene.**

Some important characteristics of the free radicals are :

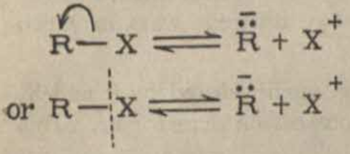
1. They exhibit paramagnetism due to the presence of one or two unpaired electrons. Detection of the free radicals is usually made by utilising this property.

2. Free radicals are extremely reactive and undergo addition **reactions.**

3. When a free radical is more or less **stable,** it owes its **stability** to resonance or mesomerism among the possible resonating forms.

(ii) The second way by which an electron-pair covalent bond R – X can be broken, involves unequal redistribution of the bond-pair between R and X. Such an **electron-pair unsharing** process or breaking of a covalent bond, in which the bond-pair is retained by one or the other atom or groups of atoms, is called **heterolysis** or **heterolytic fission.** A heterolytic fission can proceed in two ways, (a) and (b) :

(a) Both the electrons of the bond-pair are retained by R (see below).

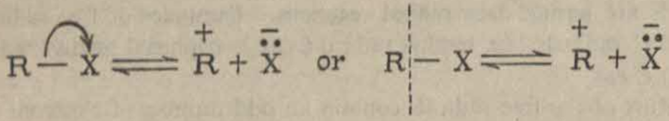


$$R-X \rightleftharpoons \overset{-}{\ddot{R}} + \overset{+}{X}$$

or $$R-\vdots X \rightleftharpoons \overset{-}{\ddot{R}} + \overset{+}{X}$$

If R is an alkyl group like the methyl group (or an aryl group like the phenyl group), the carbon atom of the $CH_3$ group carries the negative charge and is known as a **carbanion.** A carbanion is a highly reactive species and due to the presence of a non-bonded electron-pair along with a negative charge, it is attacked by reagents which seek high electron density centres. Thus, in this case (in the reaction $Y+R-X=R-Y+X$), Y is called an **electrophilic** reagent or an **anionoid** reagent, as it attacks $\ddot{C}H_3$ at the point of high electron density. Needless to say that $\ddot{C}H_3$ itself is a **nucleophile,** since it seeks a low electron density centre to which it can bind itself and release its negative charge and high electron density.

(b) The bond pair is retained by X :



$$R-X \rightleftharpoons \overset{+}{R} + \overset{-}{\ddot{X}} \quad \text{or} \quad R\vdots-X \rightleftharpoons \overset{+}{R} + \overset{-}{\ddot{X}}$$

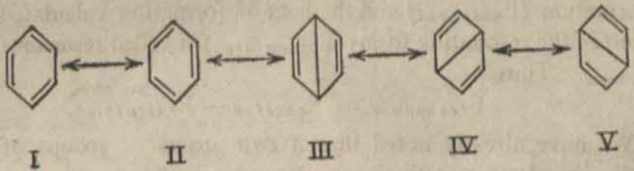
If $R^+$ is a group, with carbon atom carrying the positive charge, like $\overset{+}{C}H_3$, then the group $R^+$ is called a **carbonium ion.** A carbonium ion is electron-defficient and lacks a pair of electrons in the valency-shell of the carbon atom. Thus, a carbonium ion is a strong **electrophile** and seeks a high electron density centre. It is attacked by reagents which are electron-rich and seek positive charges or low electron density centres. In such a case, where $R^+$ is a carbonium ion, the reagent Y (in reaction 5.1) is called a **nucleophilic** or **catenoid** reagent.

## Electron displacements in a covalent molecule and consequent changes of fundamental importance.

### Resonance or mesomerism.

Before entering into a discussion about the nature of the covalent bond, one must be somewhat familiar with the principle of **resonance** or **mesomerism**. This principle is an essential outcome of quantum mechanical considerations of electronic structures of molecules and their energy-content, and is best understood through mathematical treatment. We will make a modest attempt here to present the physical concept underlying this principle.

Often it so happens that the **extra-stability** and many other associated properties of a molecule (such as polarity, bond-length, chemical reactivity *etc.*) cannot be completely explained by any single electronic structure. Benzene is a good example of such a case. Such molecules may, in principle, be represented as a **hybrid** of several closely related electronic structures, each of which can explain majority of the properties but none is capable of explaining all. The different possible structures are called *resonating forms* and they are said to **resonate** (extremely rapid interchange) among themselves, resulting in a considerable lowering of energy of the **resonance hybrid** —the actual state in which the molecule exists. Thus, benzene is most conveniently represented as a resonance hybrid of the following structures I—V ; the major contributors being the symmetrical structures I and II (about 80%). It is only in this manner that the bond lengths, stability towards oxidation, reduction, addition *etc.* and many other properties of benzene can be explained.



However, it must be kept in mind while formulating or choosing the possible resonating structures that the following conditions* must be satisfied by the canonical forms for resonance to occur between them.

(1) The relative positions of the various constituent atoms must be the same in all the canonical forms between which resonance may occur.

(2) The individual forms differ only in the distribution of the valence electrons around the different nuclei.

(3) The different forms must be equivalent or nearly equivalent with little difference in energy-content in order that they may effectively contribute to resonance.

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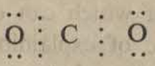
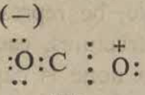
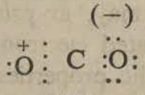
[*] These conditions were first envisaged by Pauling in his famous book "Nature of the Chemical Bond".

(4) The different forms must have the same number of unpaired electrons.

As a result of resonance, the energy of the *resonance hybrid* or the actual state in which the molecule exists, is considerably lowered in comparison to the energy of the resonating form which has the lowest energy. Due to this lowering of energy, the resonance hybrid becomes stabler than any one of the resonating structures. Carbon dioxide may be represented by the following three canonical forms, satisfying the conditions mentioned before :


(I)


(II)


(III)

The heat of for mation of carbon dioxide, found experimentally, is greater than the correspondingc alculated value by 31·6 Kcal. Thus, the $CO_2$ molecule requires 31·6 Kcals more energy to break it up into carbon and oxygen than what is expected from its structure O=C=O. This difference between the actual or experimentally obtained heat of formation ($E_{observed}$) and the heat of formation calculated for the stablest of the resonating forms ($E_{calculated}$) is called **resonance energy,** $E_{resonace}$. Thus,

$$E_{resonance} = E_{observed} - E_{calculated}.$$

We have already noted that if two atoms or groups of atoms, differing in electronegativity, are bound together by an electron-pair covalent bond, the bond pair is somewhat displaced towards the more electronegative atom or group, resulting in partial ionic character. This is manifested in the appearance of **dipole moments** in such compounds.

**Inductive effect** is another type of manifestation of **partial electron displacement of permanent nature,** while a **transient but complete transfer** of a pair of electrons, shared between two atoms, to the more electronegative atom is called an **electromeric effect.**

## Inductive effect.

Let us consider a molecule like n-butyl chloride,

$$CH_3.CH_2.CH_2.CH_2.Cl,$$

in which the electronegative atom chlorine is bound at one end of the carbon chain, $C_4-C_3-C_2-C_1-Cl$. The chlorine atom, being more electronegative than carbon (Pauling electronegativity value for carbon=2·5 and for Cl=3·0), the bond-pair between $C_1$ and Cl will be displaced towards the chlorine atom. As a result, the chlorine atom will be slightly negatively charged while the $C_1$-carbon will acquire a small positive charge. This may be represented as in fig. (A) below :

$$\underset{(A)}{-\overset{\delta_1+}{C_1} \rightarrow \overset{\delta-}{Cl}} \qquad \underset{(B)}{\overset{\delta_4+}{C_4} \rightarrow \overset{\delta_3+}{C_3} \rightarrow \overset{\delta_2+}{C_2} \rightarrow \overset{\delta_1+}{C_1} \rightarrow \overset{\delta-}{Cl}}$$

Now, the presence of the small positive charge $\delta_1+$ on $C_1$ will induce it to attract the bond-pair between $C_1$ and $C_2$ towards itself. As a result of this, another small positive charge $\delta_2+$ will accumulate on the carbon atom, $C_2$. This effect is transmitted throughout the chain of carbon atoms, creating small positive charges $\delta_3+$ and $\delta_4+$ on $C_3$ and $C_4$ respectively (fig. B). Such an electron displacement of **permanent** nature along a carbon chain is known as **inductive effect.** It is quite obvious that $\delta_1+$ is greater than $\delta_2+$ which is greater than $\delta_3+$, i.e. $\delta_1+ > \delta_2+ > \delta_3+ > \delta_4+$. Inductive effect decreases rapidly with distance from the electronegative atom and becomes negligible after the second carbon atom ($C_2$) for all practical purposes.

For the evaluation of the relative inductive effects of different atoms or groups, the standard substance chosen is the hydrogen atom in the standard molecule $R_3C—H$. If in a molecule $R_3C—Z$ (obtained by the replacement of the hydrogen atom of the molecule $R_3C—H$ by Z), the electron-density on the portion $R_3C$ is decreased than the electron-density originally present on $R_3C$ in the standard molecule $R_3C—H$, the atom or group Z is said to possess a **–I effect. Thus,** all atoms or groups which are more electron-attracting than hydrogen have **–I effect.** Hence, all atoms or groups which are less electron-attracting or more electron-repelling than hydrogen are said to possess a **+I effect.** The inductive effect is generally represented as

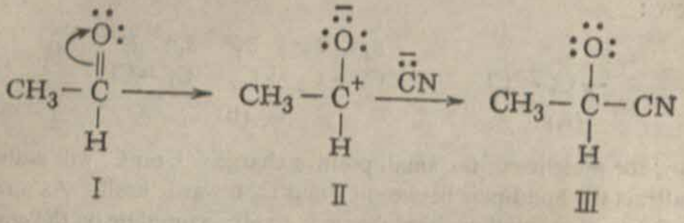
$$C_4 \rightarrow —C_3 \rightarrow —C_2 \rightarrow —C_1 \rightarrow X$$

Inductive effects of the more familiar atoms or groups may be arranged in the following order :

$$\underset{\xleftarrow[\text{increases}]{\qquad\qquad\qquad}}{\underset{-I}{NO_2 > F > Cl > Br > I > OCH_3 > C_6H_5}} > H > \underset{\xrightarrow[\text{increases}]{\qquad\qquad\qquad}}{\underset{+I}{CH_3 > C_2H_5 > (CH_3)_2CH > (CH_3)_3C}}$$

## Electromeric effect.

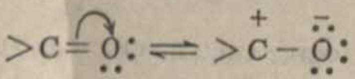
Let us consider a very common reaction. An aldehyde, say acetaldehyde, adds up hydrogen cyanide to form acetaldehyde cyanohydrin. Hydrogen cyanide first splits up into $H^+$ and $CN^-$ and then the carbonyl group of the acetaldehyde molecule undergoes the following electron rearrangement :



forming the carbonium ion which is then attacked by the nucleophilic agent $\overset{-}{\text{C}}$N.

Here we find that the carbonyl carbon atom is bound to the more electronegative oxygen by a double bond (multiple covalent bond). At the moment of reaction, the oxygen atom takes complete control of one of the bond-pairs. The carbon atom, losing its share of that bond-pair, acquires a positive charge, while the oxygen atom, getting one more electron than its due, becomes negatively charged, and the acetaldehyde molecule assumes the structure II.

Such an effect, involving the complete transfer of a shared pair of electrons from one atom (the carbonyl carbon atom) to the other atom (the carbonyl oxygen atom) joined by a double or a triple bond, is called **electromeric effect.** It must be mentioned here that this is a **temporary effect** and comes into play only at the requirement of the attaking nucleophilic reagent. In otherwords, since the nucleophile cyanide ion requires a positively charged or low electron-density centre, the carbonium ion is created by the operation of the electromeric effect. If the attacking reagent is removed, the electromeric effect is reversed and the molecule is reverted to its original structure. The electromeric effect is represented as :



$$>C=\ddot{\underset{\cdot\cdot}{O}}: \rightleftharpoons >\overset{+}{C}-\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:$$

and the electron-pair shift generally operates towards the more electronegative element from the less electronegative one.

**Bond length.**

It has been proposed that the length of a covalent bond X–Y is the sum of the covalent radii of the atoms X and Y. Thus, the length of the bond X–Y is equal to $r_x+r_y$, where $r_x$ and $r_y$ are the covalent radii of X and Y in their normal oxidation states. The carbon-carbon bond length ($r_{c-c}$) in ethane and the chlorine-chlorine bond length ($r_{cl-cl}$) in the chlorine molecule can thus be utilised to calculate the carbon-chlorine bond length ($r_{c-cl}$) in the carbon tetrachloride molecule.

$$r_{c-c} = 1{\cdot}54\ \mathring{A} \quad \therefore \quad r_c = \frac{1{\cdot}54}{2} = 0{\cdot}77\ \mathring{A}$$

$$r_{cl-cl} = 1{\cdot}98\ \mathring{A} \quad \therefore \quad r_{cl} = \frac{1{\cdot}98}{2} = 0{\cdot}99\ \mathring{A}$$

Hence, $r_{c-cl} = 0{\cdot}77 + 0{\cdot}99 = 1{\cdot}76\ \mathring{A}$.

The actual bond length C—Cl in $CCl_4$ has been experimentally found to be 1·76 Å.

The agreement of this calculated value with the observed value shows that **the concept of additivity of covalent radii** in simple molecules involving covalent bonding is a valid one. Table 3·4 contains the values of the covalent radii of some atoms in different chemical environments.

TABLE 3.4

**Covalent radii of some atoms in simple molecules (Å)**

| Atom | Single | Double | Triple |
|---|---|---|---|
| H | 0·37 | — | — |
| B | 0·81 | 0·71 | 0·64 |
| C | 0·77 | 0·67 | 0·60 |
| Si | 1·17 | 1·07 | 1·00 |
| N | 0·74 | 0·62 | 0·55 |
| P | 1·10 | 1·00 | 0·93 |
| O | 0·74 | 0·62 | 0·55 |
| S | 1·04 | 0·94 | 0·87 |
| F | 0·72 | — | — |
| Cl | 0·99 | 0·89 | — |
| Br | 1·14 | 1·04 | — |
| I | 1·33 | 1·23 | — |

However, it must be kept in mind that the concept of additivity of the covalent radii in obtaining the bond distance, is not fully applicable in all types of molecules, as several other structural factors affect bond lengths and produce quite appreciable variations from one molecule to another. The most important factors which affect bond lengths are :

(1) Resonance (and other types of electron delocalisation processes), (2) Electronegativity and (3) Hybridisation.

(1). *Effect of Resonance* : While discussing about resonance, we have already pointed out that the actual structure of a molecule is a hybrid of the possible resonating structures, some of which may possess more multiple bond character than the others. Since the double bonds are shorter than the single bonds and the triple bonds are even shorter than the double bonds, the observed bond length will depend on the relative contribution of the different resonating forms in the actual structure of the molecule. As a relevant example, we can cite the case of the sulphate ion, where the observed S—O distance is 1·51Å, compared to the sum of the covalent radii of sulphur and oxygen, which comes to 1·78Å. The observed C—O bond distance in carbon dioxide is 1·15Å which is less than the calculated C—O bond distance of 1·29Å. Such deviations are due to the contributions of the multiple bonded resonating structures of the sulphate ion and the carbon dioxide molecule.

(2). *Effect of Electronegativity* : If the electronegativity of the carbon atom in $>C-X$ increases by the presence of electron-withdrawing atoms or groups on it, the length of the C—X bond contracts. Thus, the $X_3C-X$ bond is always shorter than the $H_3C-X$ bond, where X=F, Cl and Br. The data in Table 3.5 will bear out this statement.

TABLE 3.5

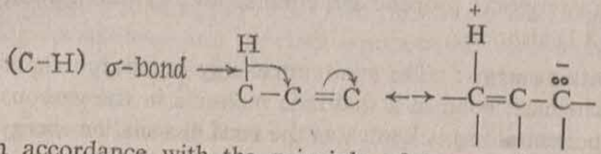
| C—H (Å) | | C—F (Å) | | C—Cl (Å) | |
|---|---|---|---|---|---|
| $CH_3.CH_2-H$ | 1·102 | $H_3C-F$ | 1·391 | $H_3C-Cl$ | 1·780 |
| $CH_3-H$ | 1·094 | $F_3C-F$ | 1·323 | $H_2ClC-Cl$ | 1·772 |
| $Cl_3C-H$ | 1·06 | | | $HCl_2C-Cl$ | 1·763 |
| | | | | $Cl_3C-Cl$ | 1·755 |
| | | | | $F_3C-Cl$ | 1·72 |

(3). *Effect of Hybridisation* : Bond lengths of the C—H, C—X(X=Cl, Br) and similar single bonds change with the state of hybridisation of the carbon atom. Table 3.6 illustrates this point quite clearly.

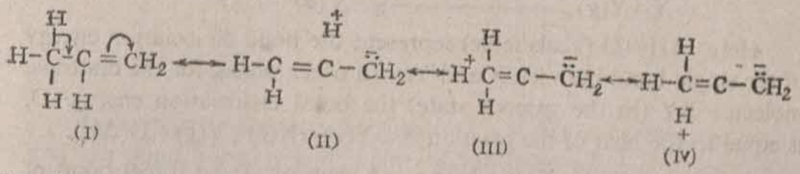
TABLE 3.6

| Hybridisation type of the carbon atom | C—H bond length Å | C—Cl bond length Å | C—Br bond length Å |
|---|---|---|---|
| $sp^3$ | 1·095 | 1·771 | 1·927 |
| $sp^2$ | 1·071 | 1·711 | 1·875 |
| $sp$ | 1·058 | 1·631 | 1·795 |

*Hyperconjugation* : When an alkyl group (e.g. $CH_3$ group) is attached to an unsaturated carbon atom (e.g. C=C or C≡C), the system is stabilised through the operation of a special type of resonance known as *hyperconjugation*. In such cases, σ-electrons of the H−C bond becomes less localised in the following manner :



In accordance with the principle of hyperconjugation, structure of propene ($CH_3-CH=CH_2$) is best represented as a resonance hybrid of the following hyperconjugating forms :



Involvement of each of the three (C−H) σ-bonds of the methyl group in hyperconjugation can be visualised from the ionic structures (II)—(IV). In each of the resonating forms (II), (III) and (IV), one of the three (C−H) σ-bonds is shown to be broken. This is why *hyperconjugation* is also referred to as *no-bond resonance*. It is also known as *Baker-Nathan effect*, named after its discoverers. But, it should be appreciated that the H-atom of each of the three (C−H) σ-bonds participating in hyperconjugation with the C=C double bond *are not truly free* and the relative positions of the C and H atoms of the methyl group are not changed significantly. The true effect of hyperconjugation is to enhance the ionic character of the (C–H) σ-bonds involved in hyperconjugation and consequent delocalisation of the (C–H) σ-bond electrons. Extra stability of a molecule in which hyperconjugative effect is in operation comes because of the resonance between the covalent and the ionic structures.

Effect of hyperconjugation is manifested in the shortening of (C–H) σ-bonds involved in hyperconjugation.

| | | |
|---|---|---|
| $H_3C—CH_3$ | $H_3C—CH{=}CH_2$ | $H_3C—C{\equiv}CH$ |
| 1·54 Å | 1·50 Å | 1·46 Å |
| Ethane | Propene | Methyl acetylene |

Due to hyperconjugation the $H_3C-C$ bond in propene is shorter than the $H_3C-C$ bond of ethane. For similar reasons, the $CH_3-C$ bond in methyl acetylene is also shorter than that of ethane.

Enhancement of stability of a system due to hyperconjugation is reflected in the values of the (C–H) σ-bond dissociation energies of propene and ethane. The relative values of the comparable (C–H) σ-bond dissociation energies of propene and ethane indicates stabilisation of propene by ~8 kcals/mole.

**Bond dissociation energy** : The minimum energy necessary to split up a particular chemical bond in a diatomic molecule in the gaseous state to the component atoms is known as the **bond dissociation energy** (D) of the bond in question. This energy is expressed generally in kcals/mole.

$$X-Y(g) \xrightarrow{+\ \Delta H \text{ (energy)}} X(g)+Y(g)^*$$

Here $\Delta H = D$ (kcals/mole) represent the bond dissociation energy of the single bond between X and Y. In other words, for the diatomic molecule XY (in the gaseous state) the bond dissociation energy, D, is equal to the heat of the reaction $X-Y(g)=X(g)+Y(g)+D(\Delta H)$.

In molecules like $NH_3$ where more than one (here three) bond of the same type (here N–H bonds) are present, the average value of the bond dissociation energies of the three N–H bonds is taken as the bond dissociation energy of a N–H bond, $D_{N-H}$. But it is to be remembered that bond dissociation energies of each individual N–H bond are not exactly equal. Because, after the dissociation of the first

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* It is assumed that the molecule XY and the atoms are all present in the ground state and that bond dissociation energies do not vary significantly with temperature.

N – H bond, the nature of the remaining two N – H bonds will definitely be changed to some extent. The stepwise dissociation of the three N – H bonds may be represented as :

$$NH_3(g) \longrightarrow NH_2(g) + H(g) + \Delta H_1$$
$$NH_2(g) \longrightarrow NH(g) + H(g) + \Delta H_2$$
$$NH(g) \longrightarrow N(g) + H(g) + \Delta H_3$$

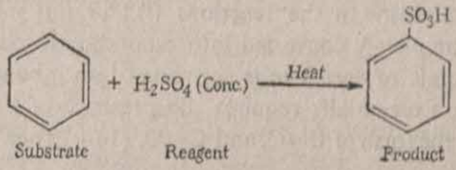
It is clear that $\Delta H_1$, $\Delta H_2$ and $\Delta H_3$ are not equal to one another. But it is true that $\Delta H_1 + \Delta H_2 + \Delta H_3 = 3\, D_{N-H}$.

**Classification of organic reactions**

In an organic reaction one or more covalent bonds present in the reactant molecules are broken and new bonds are formed subsequently or simultaneously leading to the formation of new organic compounds. When two reactants take part in an organic reaction, one is called the **substrate** and the other is known as the **reagent**. Thus, an organic reaction can be represented as

**Substrate + Reagent ⟶ Products.**

Of the two reactants, if one is a carbon compound while the other is a compound of any other element, *the carbon compound is regarded as the* **substrate** and the other compound is considered as the reagent. In the sulphonation reaction of benzene in which benzene is converted to benzene sulphonic acid by heating with concentrated $H_2SO_4$, benzene is the substrate while $H_2SO_4$ is the reactant.



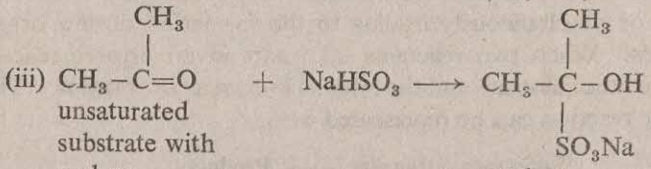
In an organic reaction the substrate is always a carbon compound and the bond breaking and bond making takes place at one or more carbon atoms of the substrate.

Depending on their characteristic features, various types of organic reactions utilised for the synthesis of different classes of organic compounds are generally divided into the following three general types :

(A) **Addition reactions,** (B) **Elimination reactions** and (C) **Substitution reactions.**

(A) **Addition reactions :** Reactions in which new atoms or groups (obtained from the reagent) are added up to an unsaturated centre (e.g. double or triple bonds) of the substrate are called **addition reactions.** Examples of a few well-known addition reactions are given below.

| | | | | |
|---|---|---|---|---|
| (i) $H_2C=CH_2$ | + | $Br_2$ | $\longrightarrow$ | $BrCH_2-CH_2Br$ |
| unsatured<br>substrate<br>(ethylene) | | reagent | | saturated product<br>(dibromo ethane) |
| (ii) $HC\equiv CH$ | + | $H_2$ | $\longrightarrow$ | $H_2C=CH_2$ |
| unsaturated<br>substrate<br>(acetylene) | | reagent | | less unsaturated<br>product<br>(ethylene) |



$$\text{(iii)}\ CH_3-\overset{CH_3}{\overset{|}{C}}=O \quad + \quad NaHSO_3 \longrightarrow CH_3-\underset{SO_3Na}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$$

| | |
|---|---|
| unsaturated<br>substrate with<br>carbon-<br>oxygen double<br>bond (acetone) | product<br>saturated with carbon-<br>oxygen single bond |

From the above examples of addition reactions it can be clearly understood that as a result of addition reaction *extent of unsaturation in the substrate is decreased.* In other words as a result of addition reaction π-bonds present in the substrate are converted, wholly or partially, to σ-bonds. In the reactions (i) and (iii) π-bonds of the substrate are completely converted into σ-bonds. In reaction (ii) one of the two π-bonds of acetylene is converted into σ-bonds. Thus, an addition reaction essentially requires the presence of unsaturation in the substrate in the form of C=C, and C=O, (1σ+1π) or C≡C, C≡N (1σ+2π) etc.

(B) **Elimination reactions :** Reactions, in which two atoms/groups or one group and an atom are simultaneously removed from a substrate molecule, are called **elimination reactions.** A few common elimination reactions are cited below .

| | | |
|---|---|---|
| (i) $CH_3-CH_2-CH_2I+KOH$ | $\longrightarrow$ | $CH_3-CH=CH_2+KI+H_2O$ |
| Saturated<br>substrate<br>(all σ-bonds) | reagent | Unsaturated product<br>(one π-bond) |

In this reaction one H and one I atom of the substrate are eliminated, leading to the formation of a π-bond.

(ii) $ICH_2-CH_2I + Zn \xrightarrow[\text{heat}]{\text{ethanol solution}} H_2C=CH_2 + ZnI_2$

Saturated substrate (all σ-bonds) — reagent — Unsaturated product (one π-bond)

In this reaction 2 atoms of I are removed.

(iii) $CH_3-CH_2-HSO_4 \xrightarrow{\text{heat}} H_2C=CH_2+H_2SO_4$

Saturated substrate (σ-bonds) — Unsaturated product (one π-bond)

In this reaction one H-atom and the $HSO_4$ group are eliminated simultaneously.

An examination of the above reaction clearly shows that when a substrate undergoes an elimination reaction, unsaturation is generated in it. In other words some of the σ-bonds present in the substrate are converted into π-bonds. Hence it can be said that elimination reactions possess the opposite characteristics of addition reactions.

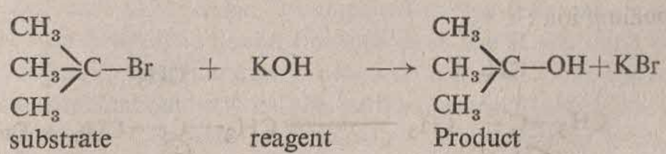
(C) **Substitution reactions :** Reactions in which one or more atoms or groups present in the substrate are removed and some other atoms/groups take their position, are known as **substitution reactions.** Following are three examples of such substitution reactions.

(i) $CH_3Cl + KCN \rightarrow CH_3CN + KCl$

substrate — product

In this reaction the Cl-atom of $CH_3Cl$ has been replaced or substituted by the $-CN$ groups. In other words, after this reaction a $(C-Cl)$ σ-bond has been converted to a$(C-CN)$ σ-bond. In this case the Cl is known as the **leaving group.**

(ii)

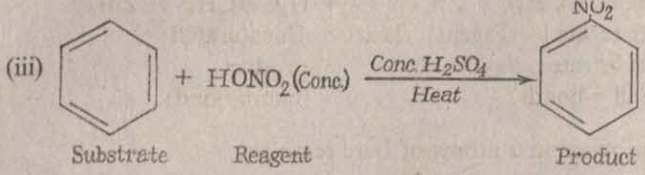


$$(CH_3)_3C-Br + KOH \longrightarrow (CH_3)_3C-OH + KBr$$

substrate (t-butyl bromide) — reagent — Product (t-butyl alcohol)

In this reaction Br-atom of the tertiary butyl bromide molecule (substrate) is substituted or replaced by the $-OH$ group of the reactant KOH. In other words, due to this substitution reaction the $(C-Br)$

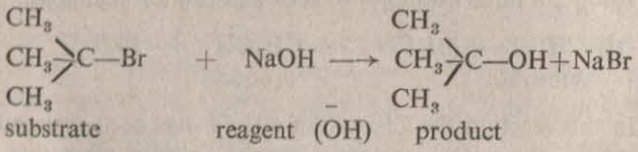
σ-bond of tertiary butyl bromide is transformed into a (C – OH)σ-bond. In this reaction Br is the **leaving group.**

(iii)


In this reaction one hydrogen atom of the benzene ring is replaced by a $-NO_2$ group and one (C – H) σ-bond of the substrate (benzene) is converted into a ($C-NO_2$) σ-bond of the product nitrobenzene.

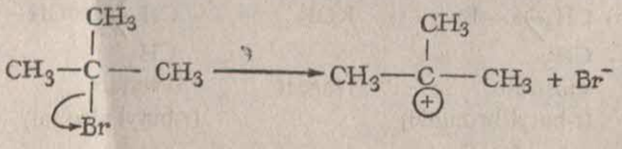
**Classification of substitution reactions :** Depending on the mechanism involved substitution reactions are classified into [A] **nucleophilic substitution** and [B] **electrophilic substitution.**

[A] **Nucleophilic** (nucleus seeking) **substitution reactions** ($S_N$ reactions) : When a nucleophilic reagent like $^-OH$, $^-OR$, $^-CN$ etc. takes part in a substitution reaction, the reaction is termed as **nucleophilic substitution.** Such reactions are expressed in the abbreviated form $S_N$, in which '*S*' stands for *substitution* and '*N*' stands for the word *nucleophilic*. Of the three examples of substitution reactions, (i) and (ii) are nucleophilic substitution reactions. In those two reactions the nucleophilic reagents are $^-OH$ and $^-CN$. Example of another nucleophilic substitution is given below :

(iv)


$$\underset{\text{substrate}}{\underset{CH_3}{\overset{CH_3}{CH_3\!>\!C-Br}}} + \underset{\text{reagent }(\overset{-}{OH})}{NaOH} \longrightarrow \underset{\text{product}}{\underset{CH_3}{\overset{CH_3}{CH_3\!>\!C-OH}}} + NaBr$$

In this reaction $^-OH$-ion (generated by the dissociation of NaOH, $NaOH \rightleftharpoons Na^+ + OH^-$) is the nucleophilic reagent. The (C – Br) bond of the substrate first undergoes *heterolytic fission* generating the tertiary carbonium ion :



$$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_3 + Br^-$$

Thereafter the negatively charged nucleophilic reagent $^-OH$ combines with the positively charged tertiary carbonium ion forming the product $(CH_3)_3C-OH$.

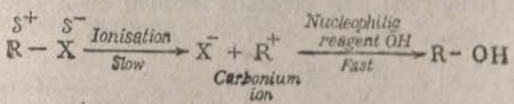
*When the rate of such a* S*N-reaction depends on the concentration of only the substrate or that of the reactant, the reaction under examination is known as* $S_N1$-reaction. This symbol indicates that this reaction is a nucleophilic substitution whose molecularity is 1. The reactions (ii) and (iv) represent such SN1 reactions.. In both of those reactions, the rate determining step is the ionisation of tert-butyl halide : $(CH_3)_3{}^{-}C-X \rightarrow (CH_3)_3C^{+}+X^{-}$ and the rate of this ionization reaction depends on the concentration of the $(CH_3)_3C-X$ only. Hence, molecularity of these reactions is 1. Thus we can conclude that the reaction

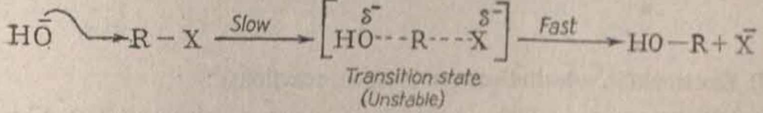
$$(CH_3)_3C-X+{}^{-}OH \longrightarrow (CH_3)_3C-OH+X^{-}$$

is definitely a $S_N1$ reaction.

Following similar arguments, *in a* SN2 *reaction the rate of the rate determining step depends on the concentrations of both the substrate and the reactant.*

It has been found that hydrolysis of an alkyl halide R—X by the action of a very strong nucliophile like ⁻OH (KOH or NaOH) can occur through both *SN*1 and *SN*2 pathways. Three factors, (i) nature of the carbonium ion, (ii) concentration of the nucleophilic reagent and (iii) polarity of the medium in which the reaction takes place determines whether the reaction will go through the *SN*1 or the *SN*2 pathways. These two possible pathways (*SN*1 and *SN*2) through which the hydrolysis of an alkyl halide (R – X) by – OH can occur are schematically shown below :

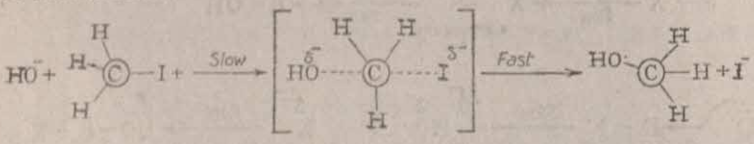




In the first case the reaction is completed in two different steps. In the first step heterolytic fission (ionisation) of the R – X bond occurs slowly leading to the generation of the carbonium ion. In the second step the combination between the carbonium ion (electrophile) and the nucleophile ⁻OH takes place *rapidly*. As the rate of ionisation, which is slow, depends on the concentration of only the substrate R – X, this hydrolysis is definitely a *SN*1 reaction. Examples of *SN*1 reactions (ii) and (iv) are already mentioned. In the second case also the first step is the rate determining (slow) step, in which a *transition state* is created involving the substrate and the reactant simultaneously. In this *transition state* both the substituent $^-OH$ and the leaving group X are rather loosely bound to the reaction centre (carbon atom) through partial or transient bonds indicated by the (- - -) sign. In the transition state, the C–X bond is not completely broken and the C–OH bond is not fully formed as well. The incoming substituent $^-OH$ and the leaving group X keeps contact with the carbon atom reaction centre, themselves remaining as far from each other as possible. In this transition state the C - - - OH and C - - - X distances are much larger than the normal C–OH and C–X bond lengths. The rate of formation of such a transition state depends on the concentration of both R–X and $^-OH$. Hence the reaction under consideration definitely falls in the *SN*2 category. In the second step the transient C - - - OH bond gradually becomes a normal C–OH bond when the –OH group moves closer to the carbon atom. At the same time the I atom involved in the C - - - X transient bond moves away from the carbon atom resulting in the formation of the ion $X^-$ as a separate entity.

It has been noted that when the alkyl radical of R–X is a tertiary alkyl radical the hydrolysis reaction proceeds through *SN*1 pathway and (ii) when R is a primary alkyl radical the hydrolysis reaction takes the *SN*2-pathway. In the case of R being a secondary alkyl radical, the reaction can proceed through any one of *SN*1 or *SN*2 pathways.

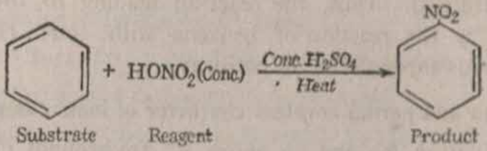
From the above discussion it is evident that the hydrolysis of methyl iodide ($CH_3I$) by $^-OH$ ions proceeds through *SN*-2 pathway as shown below.



**(B) Electrophilic substitution reactions** (SE-reactions) :

Reactions in which electrophilic reagents (electrophiles) like $\overset{+}{N}O_2$, $\overset{+}{S}O_3H$ react with a substrate and replace one or more atoms or groups present in the substrate are named **electrophilic substitution reactions.** Such electrophilic substitution reactions are abbreviated as SE (S for substitution and E for electrophilic). Rate determining step of a SE reaction always depends on the concentrations of both the substrate and the reagent. Hence, *S*E reactions are bimolecular reactions, i.e. molecularity of *S*E reactions is 2. Thus, *SE* reaction takes place through a pathway which is similar to the *SN*2-pathway, discussed before.

In the first step of a *SE* reaction, (which is the rate determining step) a transition state involving both the substrate and the electrophilic reagent is generated. Rate of formation of this transition state is dependent on the concentration of the substrate as well as that of the nucleophile. In the next step an atom or group of the substrate goes off and the electrophile takes its place simultaneously. Nitration of benzene by conc. $HNO_3$ in presence of conc. $H_2SO_4$ is a familiar example of electrophilic substitution.

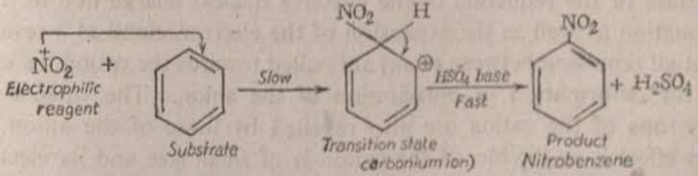


In the above reaction one H-atom of benzene is substituted by one $-NO_2$ group.

Generation of the electrophilic reagent $-\overset{+}{N}O_2$ by the reaction of conc . $HNO_3$ and conc . $H_2SO_4$ may be represented as follows :

$$\mathrm{HONO_2+2H_2SO_4 \longrightarrow \underset{\substack{\text{electrophilic}\\ \text{reagent}}}{\overset{+}{N}O_2}+H_3\overset{+}{O}+\underset{(\text{base})}{2HS\overset{-}{O}_4}}$$

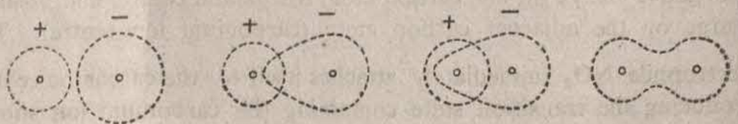
This $\overset{+}{N}O_2$ cation is a strong electrophile, and reacts with the benzene nucleus and forms nitrobenzene by the replacement of one H-atom through the *S*E pathway as shown below:



It can be visualised from the above reaction scheme that in the first step of the reaction the nucleophile $\overset{+}{N}O_2$ is attracted by the $\pi$-electron cloud of benzene as a result of which one of the three $\pi$-bonds of benzene undergoes heterolytic fission resulting in the accumulation of negative charge on one carbon atom (carbanion centre) and positive charge on the adjacent carbon atom (carbonium ion centre). The electrophile $\overset{+}{N}O_2$ immediately attaches itself to the carbanion centre, producing the transition state containing the carbonium ion shown above. Formation of this transition state is the rate determining step and its rate is dependent on the concentration of both benzene (substrate) and $\overset{+}{N}O_2$ group (nucleophile). In the transition state the hydrogen atom attached to the same carbon atom to which the nucliophile $\overset{+}{N}O_2$ has attached itself, is removed as $H^+$ with the help of the $HS\overline{O}_4$ ion acting as a base and forming $H_2SO_4$. The electron pair of this broken C–H bond re-forms the third double bond of the benzene nucleus as a result of which the +ve charge on the adjacent carbon atom is neutralised. Thus, the reaction leading to the formation nitrobenzene by the reaction of benzene with conc. $HNO_3$-$H_2SO_4$ mixture proceeds through the *SE* pathway.

**Ionic distortion and partial covalent character of ionic compounds.**

When a cation $A^+$ and an anion $B^-$ are brought close to each other, the nature of the chemical bond between them will depend on the resultant effects of their mutual interactions. That chemical bonds ranging from purely ionic to predominantly covalent can result from interactions between anions and cations, is evident from the properties of compounds like NaCl, $HgI_2$, AuCl etc. The way in which covalent character creeps into the ionic bonds has been explained by Fajan in a set of generalizations based on deformation of the valence-shell of the anion by the positively charged field of the cation. These generalizations are often known as **Fajan's Rules.** Fajan proposed that, when brought in the vicinity of the cation, the valence-shell electrons of the anion (which are rather loosely bound because of the reduction of the effective nuclear charge due to anion formation as well as the expansion of the electron cloud as a result of mutual repulsion between them) are pulled towards the cation, resulting in the deformation or polarisation of the anion. The valence-shell electrons of the cation are also repelled by those of the anion, but this effect is negligible, as the cation is of small size and its electrons are held very firmly due to the resultant positive charge on it. Deformation of the anion results in the inter-penetration of the valence-shell orbitals of the two ions, reducing the ionic character of the molecule. With the increasing anionic deformation, the molecule may pass into the non-polar covalent type as shown below :



Fig· 3.20

From the above figure, it is clear that, as a result of anion-deformation, a certain amount of negative charge is transferred from the anion to the cation. This decreases the electronegativity of the anionic part, with the overall result of **reduction of the electronegativity difference** of the two ions. As a direct consequence, the ionic character of the molecule, which increases with the increase in electronegativity difference (see fig. 3.19) decreases and the covalent character appears. The extent to which it occurs determines the amount of partial covalent character of the ionic bond.

**Factors influencing deformation of ions.**

Several factors favour the deformation of anions. They are :

1. **High charge on the cation and on the anion.**

High charge on the cation increases its positive charge-density which is conventionally expressed as the ratio of cation-charge and cation-radius and is termed as **ionic potential,** $\phi$. Thus, $\phi = \frac{\text{cation charge}}{\text{cation radius}}$. It is obvious that high value of $\phi$ denotes higher polarising power. Thus, $SnCl_2$ (which contains the $Sn^{+2}$ cation) is an ionic solid, while $SnCl_4$ (which contains the $Sn^{+4}$ cation) is a covalent liquid.

TABLE 3.7

| Cation | Cation radius Å | M.P. of the anhydrous chlorides (°C) |
|---|---|---|
| $Na^+$ | 0·95 | 800 |
| $Ca^{+2}$ | 0·99 | 772 |
| $Mg^{+2}$ | 0·65 | 712 |
| $Al^{+3}$ | 0·50 | Sublimes |

The data in Table 3.7 clearly shows that the melting points of the anhydrous chlorides decrease with increasing cationic charge and increasing ionic potential, which is indicative of their increasing covalent character.

High charge on the anion results in the loosening of the valence-shell electrons of the anion and the expansion of the electron-cloud due to mutual repulsion of the electrons. The more loosely the valence-electrons are bound, higher is the tendency of the anion to get polarised by a cation.

**2. Small cation.**

For cations of the same charge, a smaller radius will result in a higher value of $\phi$, which will have a greater polarising effect on a particular anion. This point is illustrated by the lower melting point of anhydrous $MgCl_2$ compared to that of anhydrous $CaCl_2$ as given in table 3.7.

**3. Large anion.**

In large anions, the outermost electronic layer is naturally more loosely bound than in one with a small size. Hence, they are much more prone to polarization. This is quite clear from the change in the melting points of the different halides of calcium given in Table 3.8.

TABLE 3.8

| Anion | Anion radius Å | M.P. of the anhydrous calcium salts (°C) |
|---|---|---|
| $F^-$ | 1·36 | 1392 |
| $Cl^-$ | 1·81 | 772 |
| $Br^-$ | 1·95 | 730 |
| $I^-$ | 2·16 | 575 |

The above data also indicate that in a group of non-metals (here Gr. VIIB), the salts of a particular cation (here $Ca^{+2}$) show increase in covalent character with the increase in the size of the monovalent anions.

**4. Cations with non-inert gas structure.**

If the charge on the cation is kept constant, the deforming capacity of the cations with an 18-electron valence-shell structure is found to be greater than that of the cations with 8-electron inert gas structure. That the melting points of the anhydrous chlorides of the coinage metals (Cu, Ag and Au) are lower than those of the corresponding salts of the alkali metals (Table 3.9), both types containing the same anion, illustrate this point.

TABLE 3.9

| Group IB<br>Eighteen-electron shell | | | GROUP IA<br>Eight-electron shell | | |
|---|---|---|---|---|---|
| Cation | Cation radius Å | Melting points of the anhydrous chlorides, °C | Cation | Cation radius Å | Melting points of the anhydrous Chlorides, °C |
| $Cu^+$ | 0·96 | 422 | $Na^+$ | 0·95 | 800 |
| $Ag^+$ | 1·26 | 455 | $K^+$ | 1·33 | 776 |
| $Au^+$ | 1·37 | 170 (decomposes) | $Rb^+$ | 1·48 | 715 |

A possible reason of the greater polarising power of the GrIB cations lies in the less shielding power of the 18-electron structure compared to that of the 8-electron configuration.

## METALLIC BOND

Importance of the study of the nature of the metallic bond becomes apparent when we note that about 70% of the known elements are metallic in character. Two important characteristics of the metals make them distinctly different from the other elements : (i) their ionization energies are smaller than the other elements (mercury is an exception) and (ii) the number of their valence-electrons are less than the number of orbitals in the valence-shell. These two characteristics are intimately related to the nature of bonding in metals.

The important physical properties that characterize metals are : (1) High electrical and thermal conductivities, (2) Bright lustrous appearence, (3) Malleability and ductility, (4) Crystal structures which are either hexagonal close-packed, cubic close-packed or body-centred cubic. The nature of bonding in metals must be able to explain the above characteristics of the metals.

Low ionization energy of a metal atom indicates that it has little affinity for extra electrons and hence, at best, a very weak covalent type of interaction between two metal atoms can occur. This explains the limited existence of diatomic molecules of Gr. IA elements like $Li_2$, $Na_2$, $K_2$ *etc.* Since interaction between two metal atoms does not lead to sufficient energy-lowering and to stability, it is possible that greater stability can be obtained if the valence-electrons of one atom move under the influence of several other nuclei. Presence of electrons fewer than the valence-orbitals in metals naturally makes this type of interaction possible. According to the accepted theory of the metallic bond, a metallic crystal consists of positive ions packed together in any one of the following geometrical arrangements : (1) Cubic close-packed (face-centred cubic), (2) hexagonal close-packed and (3) body-centred cubic, which are immersed in a cloud or sea of electrons. The negatively charged electrons hold the positive metal ions together, and since electrons and positive ions originate from neutral metal atoms, the positive and negative charges in a metal crystal are balanced. These electrons (which are the valence-electrons) are arranged in **bands of closely spaced energy-levels** and are **held in common by all the positive ions in the crystal-lattice.** A certain amount of discontinuity in the energy values exists between such different bands of electrons. These bands are termed **Brillouin Zones** and are comparable to the single quantum levels of an isolated atom. Since Pauli's exclusion principle is also operative here, the closely graded energy-levels, constituting a band, can be occupied only by two electrons of opposite spin.

Thus, the valence-electrons in a metal crystal are at the joint control of all the metal atoms in the crystal, and are rather free to move throughout the crystal-lattice and such mobility can be generated by the application of a small amount of energy. Thus, the important characteristics of the metals like high electrical and thermal conductivities, metallic lustre, malleability and ductility etc., which originate due to the presence of loosely bound and rather mobile electrons, can be readily explained. Since the electrons in a metallic crystal are more or less uniformly distributed among the constituent positive metallic ions, it is similar to the ionic bond in that they have no special directional nature. Thus, like ionic solids, the binding force in metals are spherically distributed and can act on as many members as can be packed around each metal atom in a metallic crystal. This explains the close-packed structure of the metals.

We conclude our discussion on the metallic bond by commenting that, when the number of valence-electrons in the combining atoms are less than the valence-orbitals in them, an octet or any other stable electronic configuration around each atom is not possible. In such cases, the bond between the two combining atoms become metallic in character. Thus, the metallic bond, though differing from the ionic and the covalent bonds, shares some characteristics of both of them and hence represent a transition between an ionic and a covalent bond.

## THE HYDROGEN BOND.

When a hydrogen atom is bonded to a highly electronegative atom like fluorine, the electron-pair holding the two atoms together is displaced towards the electronegative fluorine atom, giving rise to the dipolar character in the HF molecule :

$$\mathrm{H}\ \overset{\bullet\bullet}{\underset{\bullet\bullet}{:\mathrm{F}:}} \quad \text{or} \quad \overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}$$

Because of its $1s^1$ configuration, hydrogen does not possess any screening electrons. As a result, in the HF molecule, a part of the positively charged nucleus (the proton) remains exposed and this residual positive charge attracts another electronegative fluorine atom of another HF molecule, the H-atom acting as a bridge or bond between the two F-atoms which may be represented as,

$$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\cdots\cdots\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}$$

and this type of **hydrogen bonding** may be extended to several molecules. Thus, **hydrogen bond** may be defined as the force of attraction which holds two polar molecules together through the mediation of a hydrogen atom covalently bonded to an electronegative atom. Hydrogen bond is basically electrostatic in nature and is much weaker than either ionic or covalent bond. In fact, the average energy of a hydrogen bond is about 7 Kcals/mole, which is less than the value of 10 Kcals/mole representing the lower limit of the energy involved in a true chemical bond.

Because of its very small size, hydrogen can act as a bridge between not more than two electronegative atoms. Only those atoms can form hydrogen bonds which possess high electronegativity and are of small size. Thus, though chlorine and nitrogen have almost equal electronegativity, chlorine is incapable of forming hydrogen bonds, while nitrogen can do so readily.

The strength of the hydrogen bond increases with the increase in the electronegativity of the element involved in the bond and decreases in the order :

$$\mathrm{F{-}H\ldots F} > \mathrm{O{-}H\ldots O} > \mathrm{N{-}H\ldots N}.$$

Two types of hydrogen bonds are recognised, *viz.* (i) **Intermolecular** and (ii) **intramolecular**. Intermolecular hydrogen bonding gives rise to *molecular association*, resulting in the change in the magnitude of some physical properties from what is expected from their molecular weights calculated on the basis of their simple molecular formula. Thus, hydrogen bonding increases the melting points, boiling points, dielectric constants, latent heat of vaporisation, viscosity and surface tension, and decreases osmotic pressure, boiling point elevation, freezing point depression etc. Molecular association through inter-molecular hydrogen bonding in hydrofluoric acid and water are schematically shown in Fig. 3.21.

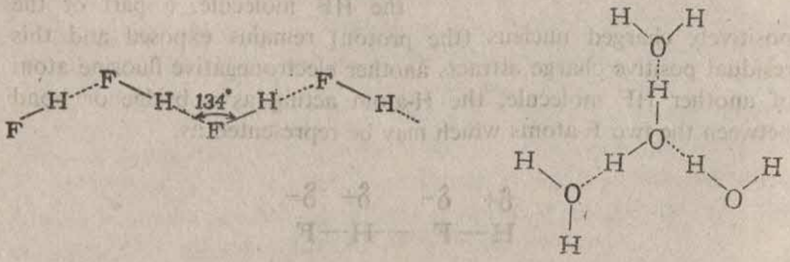
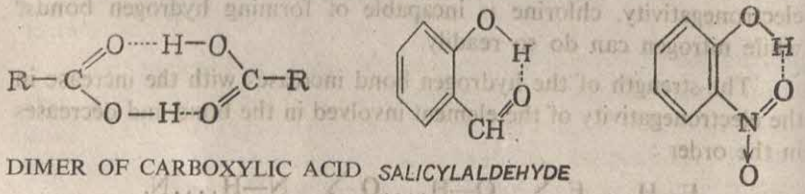


Fig. 3.21

In aqueous solution, HF dissociates as $HF \rightleftharpoons H^+ + F^-$. In a concentrated solution, the $F^-$ ion forms the bifluoride ion $[HF_2]^-$ through hydrogen bonding, and may be represented as $F^-..H—F$, which is quite stable and yields the bifluoride salts of sodium, potassium and ammonium. Since chlorine, bromine and iodine cannot form hydrogen bond, bihalides like $KHCl_2$, $KHBr_2$ and $KHI_2$ do not exist.

Intermolecular hydrogen bonding in organic compounds is found in some organic carboxylic acids leading to the formation of dimers and higher polymers (Fig. 3.22). Intramolecular hydrogen bonding is frequently encountered among organic compounds and the most common examples are ortho-hydroxy aldehydes and ortho-nitrophenols (Fig. 3.22).



DIMER OF CARBOXYLIC ACID *SALICYLALDEHYDE*

O-NITROPHENOL

Fig. 3.22

Hydrogen bonds extended through three dimension can also hold big molecules or macromolecules together in certain fixed orientations.

This aspect of hydrogen bonding is best illustrated in the Watson-Creek structure of the DNA.

*Directional character of hydrogen bonding*

It is fairly well-established that a hydrogen bond is basically electrostatic in character and is formed due to the dipole-dipole interaction (see later) as shown below :

$$\overset{\delta^-}{X}—\overset{\delta^+}{H}\ldots\overset{\delta^-}{Y}$$

where both X and Y are strongly electronegative elements like F, O or N. However, whether the bonded hydrogen atom approaches Y along any one of its hybrid orbitals containing a lone-pair is not clearly known. In most cases, hydrogen bonds do not have specific directional characteristics and the actual direction adopted can be attributed to steric requirements of the whole system. In some cases, like that of the angular $(HF)_n$ polymers, it appears that a hydrogen bond probably has some directional character.

That hydrogen bond has great significance in determining many important properties of chemical compounds has already been discussed. More recently, it has been established that, hydrogen bonding is responsible for keeping the native structure of the protein molecules, and hence, it plays a very important role in vital biological processes. In fact, the very existence of life is primarily dependent on hydrogen bonding, because, in absence of hydrogen bonding, water (having the molecular formula $H_2O$ and a molecular weight of 18) would have existed exclusively in the gaseous state, and in the absence of liquid water, life in its present form would not have come into existence at all.

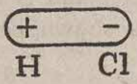
## DIPOLE BOND.

Apart from the four types of bonds discussed above, a number of other attractions among chemical entities are encountered. These are much weaker than even the hydrogen bond. All of these are of electrostatic origin and involve dipolar molecules. Dipolar molecules can attract ions and other molecules, resulting in different types of weak combinations which are not related to either electron transfer or sharing and hence, may be grouped under the general heading of **dipole bonds,** where the word **bond** is used to denote a very weak attraction. The following varieties of such **bonds** are recognised :

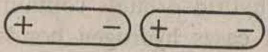
**Dipole-dipole attractions.**

We have already found that when a covalent bond is formed between two atoms differing in electronegativity, polar molecules result. Such a molecule is HCl which may be represented as :

$$\overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{Cl}} \quad \text{or}$$



Two such dipoles will attract each other and may cause a type of molecular association such as,



Such attractions are weak in nature when compared with the attractions involved in an ionic bond, but they can significantly change certain physical properties like boiling point, vapour pressure *etc.*

**Ion-dipole attractions.**

The water molecule is polar with a considerable dipole moment and is attracted by both positive and negative ions rather strongly because, an ion-dipole attraction depends on the charge on the ion and the magnitude of the electric dipole. In many cases, such as the interaction of a proton with a water molecule, leading to the formation of the hydronium ion, $H_3O^+$, the attraction is quite strong. In fact, dissolution of an ionic compound in a polar solvent results in the solvation of ions because of the operation of ion-dipole forces acting between the ions in the crystal lattice of the solid and the dipoles of the polar solvent.

**Ion-induced dipole attractions.**

Large homonuclear molecules (whose outer electrons are loosely bound), when brought in contact with a **positively** or a **negatively** charged ion, the outer electron-layer gets polarised and a dipole is said to be induced in that molecule. This induced dipole can then act on the ion, resulting in an ion-induced dipole attraction. The combination of the iodine molecule with the iodide ion represents a case of ion-induced dipole attraction : $I^- + I_2 \longrightarrow I_3^-$.

### Dipole induced-dipole attractions.

Polar molecules like the water molecule, having fairly high dipole moments, can induce dipoles in atoms or molecules whose outermost electrons are loosely bound and hence are easily deformed. These deformed species now enters into a type of very weak attractive interaction with the inducing dipolar molecule. The formation of inert gas hydrates are due to the existence of such attractions. These attractions are weaker than ion-induced dipole attractions.

### Induced dipole—induced dipole attractions.

This is the weakest among the weak electrostatic attractions being discussed. Due to the electronic motion within the neutral atom or molecule, an otherwise symmetrical molecule may develop a dipole moment which continually fluctuates in magnitude and direction. As a result, certain portion of the atom or the molecule fluctuates between a state of being positively charged and negatively charged. When such an atom or molecule is brought very near to another such atom or molecule, the fluctuating dipole of one will influence the fluctuating dipole of the other, and the positive and negative induced dipoles on adjacent atoms or molecules will attract each other. Such attractions are also termed Van der Waals forces and are responsible for causing the liquefaction of inert gases.

Keeping ourselves within the boundary of our area of operation (limited by the syllabii set by the Universities), we have now completed our discussion on **chemical bonding** and we must admit that it is a highly interesting subject but, at the same time, a complex one. We have outlined some of the most useful concepts and cited examples which will be helpful in understanding and even predicting the relation between the nature of chemical bonding and the observed chemical and physical properties of substances. However, we must also be careful to note that, the whole domain of chemistry abounds in exceptions to these generalised concepts, a glaring example of which is found in the formation of compounds of the **inert** gases by the violation of the so-called **octet rule.** So, while using these general concepts to understand a new chemical phenomenon, one must keep an open mind and apply the concepts with judicious care.

CHAPTER IV

# THE NUCLEUS AND THE PHENOMENON OF RADIOACTIVITY

## *The Story of the Inner Sphere of the Atom*

In chapter I, we have used the term **nucleus** several times and by it we meant a tiny body at the centre of the atom which contained most of the mass and all the positive charge of the atom. It is the attraction of this positively charged nucleus that keeps the extra-nuclear electrons, constituting the outer sphere of the atom, in their appropriate orbits.

### Composition of the nucleus.

From J. J. Thomson's positive ray analysis, it was established that atoms also contain positively charged particles, the smallest of which is the proton ($H^+$), having the mass of a hydrogen atom and a positive charge equal in magnitude to the electronic charge ($1 \cdot 6 \times 10^{-19}$ coulombs or $4 \cdot 8024 \times 10^{-10}$ esu). Since all the positive charges on an atom are contained in its nucleus, the proton must have come from the nucleus, *i.e.* protons are the constituents of the atomic nucleus. It was later found that the mass-number of an atom (the whole-number nearest to the experimentally determined atomic mass of an element) is always greater than the number of protons in the nucleus of an atom (hydrogen is the only exception). Rutherford (1920) therefore, predicted the existence of neutrons (particles having the mass of a proton but no charge) in the nucleus along with the protons. According to him, the mass of an atom is the sum total of the masses of the protons and the neutrons present in its nucleus. Thus, if A be the mass number of an atom and Z is its atomic number (*i.e.* number of positive charge in the nucleus, or the number of protons), then the number of neutrons present there is given by (A—Z). Thus, it was taken for granted that the nucleus of an atom is composed of neutrons and protons. The existence of neutrons in the nuclei of atoms was proved by the discovery of neutrons in 1932 by R. Chadwick. Later on, many sophisticated and powerful methods were developed by which the nuclei of various atoms were broken down and the sub-atomic particles produced thereby were studied in careful details. The impact of cosmic radiation on matter also yielded many useful informations. As a result of such experiments and careful analysis of the results, a number of **fundamental particles** were discovered. Some of the important characteristics of the more important fundamental particles are given in Table 4.1.

TABLE 4.1

Some fundamental particles and their important characteristics

| Particle | Symbol | Charge | Mass (in $C^{12}=12{\cdot}000$ scale) | Spin |
|---|---|---|---|---|
| electron | $e, e^-, \beta^-, {}_{-1}e^0$ | negative<br>$4{\cdot}8024\times10^{-10}$ esu | 0·0005486 | ½ |
| proton | $p, {}_1H^1$ | positive<br>$4{\cdot}8024\times10^{-10}$ esu | 1·007825 | ½ |
| positron | $e^+, \beta^+, {}_{+1}e^0$ | positive<br>$4{\cdot}8024\times10^{-10}$ esu | 0·0005486 | ½ |
| neutrino | $\nu$ | Zero or uncharged | 0 | ½ |
| neutron | $n, {}_0n^1$ | zero or uncharged | 1·008665 | ½ |
| neutral pi-meson | $\pi^0$ | zero | 0·1454 | 0 |
| positive pi-meson | $\pi^+$ | positive | 0·1514 | 0 |
| negative pi-meson | $\pi^-$ | negative | 0·1514 | 0 |
| positive mu-meson | $\mu^+$ | positive | 0·1152 | ½ |
| negative mu-meson | $\mu^-$ | negative | 0·1152 | ½ |

The particles in the lower half of the table are unstable and suffer further decay into one or more particles included in the first half.

Even at present, it is assumed (for all practical purposes) that the nucleus is made up of protons and neutrons held together by the mysterious nuclear forces of enormous magnitude. The particles constituting the nucleus are called **nucleons.**

### Formation of the atomic nuclei from protons and neutrons.

We will now discuss the problem involved in the gradual building up of some familiar nuclei from protons and neutrons. From Table 4.1, we see that the mass of a proton is 1·007825 mass units (relative to the mass of a $C^{12}$ nucleus, the mass of which is taken to be 12·000000). In the same atomic mass units (a.m.u.), the mass of a neutron is found to be 1·008665. First of all, we will take up the case of the formation of deuterium (${}_1H^2$ or ${}_1D^2$), the simplest nucleus containing both proton and neutron. The nucleus of deuterium, the heavier isotope* of hydrogen, is made up of one proton and one neutron and its mass, the sum of the masses of a proton and a neutron, should be

mass of proton = 1·007825 a.m.u.
mass of neutron = 1·008665 a.m.u.

mass of a proton and a neutron = 2·016490 a.m.u.

But, a very precise determination of the **isotopic** mass of deuterium indicated that its mass is 2·014102 a.m.u. Thus, there is a difference in the actual mass of the deuterium nucleus and the total mass of its constituent particles.

The difference is :

mass of a neutron + mass of a proton = 2·016490 a.m.u.
mass of a deuterium nucleus = 2·014102 a.m.u.

mass difference, $\Delta M$ = 0·002388 a.m.u.

This difference is known as the "**mass defect** or **true mass loss** and is defined as the difference in the total mass of the constituent particles and the actual mass of the nucleus in question.

**Binding energy** : The question which automatically presents itself at this point is, what happens to this mass which appears to be "*lost*" ? Now, according to Einstein's eqn. for the equivalence of mass and energy, $E = mc^2$, where E is the energy equivalent to the mass $m$ and $c$ is the velocity of light. When $m$ is expressed in grams and $c$ in cms./sec., E is expressed in ergs. The energy equivalent of one gm. of mass is then given by

$$E = 1 \times (3 \times 10^{10})^2 \text{ ergs}$$
$$= 9 \times 10^{20} \text{ ergs.}$$

---

* Isotopes are nuclei having same number of protons but different number of neutrons *e.g.* hydrogen and deuterium.

[It may be noted here that 1 a.m.u.=931 million electron volts (Mev) which is the *unit* generally used. This energy is enough to heat 500 metric tons of water at ordinary temperature to boiling.]

The mass-defect in nuclei is due to the **packing effect** of the nucleons in them. The decrease in mass during the formation of heavier nuclei from protons and neutrons is the result of the loss of corresponding amount of energy (according to Einstein's equation, $E=mc^2$), which is responsible for the stability of the nuclei formed. The observed difference between the actual mass of the constituent protons, neutrons and electrons has been expressed in the form of the **packing fraction** (Aston, 1927), which is defined as, Packing fraction $= \frac{M-A}{A}$, where M=isotopic atomic mass of the species, A=its mass number. Thus, packing fraction indicate the average mass gain or mass loss per nucleon of the particular isotope being considered in comparison to that of the $O^{16}$ nucleus. A nucleus with positive packing fraction is one which possesses excess energy, while a nucleus with negative packing fraction contains comparatively much less energy. A negative packing fraction means that the nucleus is stable, while a positive packing fraction would imply its tendency towards instability. The packing fraction of oxygen is is zero; $He^4$ and $C^{12}$ also have very low positive packing fractions and they are exceptionally stable. The lowest packing fractions (negative values) are observed for the transitional elements between Cr and Zn, but the values increase with increasing mass numbers and become positive again for mass numbers exceeding 200, indicating instability This accounts for the spontaneous disintegration (radioactivity) of such elements. The relative instability of these nuclei causes them to break up until more stable, light nuclei are formed.

The total binding energy of *an atom* is equivalent to the difference between the sum of the masses of its neutrons, protons, and extranuclear electrons and the isotopic mass.
Thus, the mass-defect of *an atom* may be written as :

$$\Delta M = Zm_H + (A-Z)m_n - M$$

where $m_H$ s the mass of the hydrogen atom (mass of proton+mass of electron), Z is the atomic number, $m_n$ is the mass of the neutron, A is the mass number and M is the exact isotopic mass. Hence, the total binding energy (B.E.) of *an atom* can be calculated as :

$$\text{B.E. (in Mev)} = 931\ [Zm_H + (A-Z)m_n - M].$$

Let us calculate the total binding energy of the neon atom (at. no. 10). Here, Z=10.

$M = 19{\cdot}99277$ amu,
$m_H = 1{\cdot}007825$ amu,
$m_n = 1{\cdot}008665$ amu,
$A = 20$.

Total B.E. of the neon atom (Mev)$=931[10\times 1{\cdot}007825+(20-10)\times 1{\cdot}008665-19{\cdot}99277]=161{\cdot}34$. Mev.

Table 4.2 contains the binding energy values of some common elements.

TABLE 4.2

*Binding energy values of some familiar elements*

| Element | Nucleus | Mass defect amu ($_8O^{16}$=16·0000 scale) | Binding energy, Mev | Binding energy, per nucleon, Mev |
|---|---|---|---|---|
| Hydrogen (Deuterium) | $_1H^2$ | 0·00235 | 2·2 | 1·09 |
| Helium | $_2He^4$ | 0·0302 | 28·12 | 7·03 |
| Lithium | $_3Li^7$ | 0·0402 | 39·12 | 5·59 |
| Beryllium | $_4Be^9$ | 0·0623 | 58·0 | 6·44 |
| Boron | $_5B^{11}$ | 0·0814 | 75·8 | 6·89 |
| Carbon | $_6C^{12}$ | 0·0986 | 91·8 | 7·66 |
| Nitrogen | $_7N^{14}$ | 0·112 | 104 | 7·46 |
| Oxygen | $_8O^{16}$ | 0·137 | 127 | 7·94 |
| Argon | $_{18}Ar^{40}$ | 0·368 | 342 | 8·57 |
| Iron | $_{26}Fe^{56}$ | 0·523 | 487 | 8·70 |
| Krypton | $_{36}Kr^{84}$ | 0·893 | 729 | 8·66 |
| Tin | $_{50}Sn^{118}$ | 1·080 | 1·011 | 8·52 |
| Xenon | $_{54}Xe^{132}$ | 1·190 | 1·110 | 8·38 |
| Lead | $_{82}Pb^{204}$ | 1·700 | 1·580 | 7·77 |
| Uranium | $_{92}U^{238}$ | 1·900 | 1·780 | 7·45 |

1 amu ($C^{12}$)=1·0003179 amu ($O^{16}$)

The energy equivalent to the mass defect of the deuterium nucleus is given by ($C^{12}$ scale)

$$E=\Delta Mc^2$$
$$E=0{\cdot}002388\times 931 \text{ Mev}$$
$$=2{\cdot}23 \text{ Mev.}$$

Thus, we find here that during the formation of the deuterium nucleus from a proton and a neutron, 0·002388 amu of mass is converted into an energy of 2·23 Mev, and this energy is called the "binding energy" of the deuterium nucleus, which holds in it the proton and the neutron together. So, to break up the deuterium nucleus into its constituents, 2·23 Mev energy must be supplied. Thus, the **binding energy of a nucleus may be defined as the energy required to break it up into the isolated nucleons.** The mass defect or true mass loss may now be defined as the mass which would be converted into energy if a particular atom is to be made up of requisite number protons and neutrons. In order to have a practical idea about the magnitude of the binding energies of various nuclei, we will convert Mev into other more familiar energy units like ergs and calories.

$$1\text{Mev} \equiv 1{\cdot}6 \times 10^{-6} \text{ ergs} \equiv 3{\cdot}8 \times 10^{-14} \text{ calories}$$

$$\therefore \quad 2{\cdot}23 \text{ Mev} \equiv 3{\cdot}568 \times 10^{-6} \text{ ergs} \equiv 8{\cdot}474 \times 10^{-14} \text{ calories}$$

Thus, if the total binding energy of 1 gm-atom of deuterium be released in some way or other, it will amount to $8{\cdot}474 \times 10^{-14} \times 6{\cdot}03 \times 10^{23}$ cals.

$$= 5{\cdot}0098 \times 10^{10} \text{ cals.} = 2{\cdot}15 \times 10^{18} \text{ ergs.}$$

From the data in Table 4.2, it is clear that the total binding energies increase with atomic mass. This is quite logical, because a nucleus with a large mass will have more nucleons to separate. However, it may be of interest to know the behaviour of the *binding energy per nucleon* with the gradual increase of the mass number. Binding energy (B.E.) per nucleon is defined as,

$$\frac{\text{total binding energy of the nucleus}}{\text{number of nucleons present in the nucleus}}$$

$$\textit{i.e.} \quad \text{B.E./nucleon} = \frac{\text{total B.E.}}{\text{mass number.}}$$

We have already found that the total binding energy of the neon nucleus is 161·34 Mev. Since the mass number of neon is 20, the binding energy per nucleon in the neon nucleus is

$$\frac{161{\cdot}34}{20} \text{ Mev} = 8{\cdot}067 \text{ Mev.}$$

A plot of binding energy per nucleon vs. mass number is shown in figure 4.1

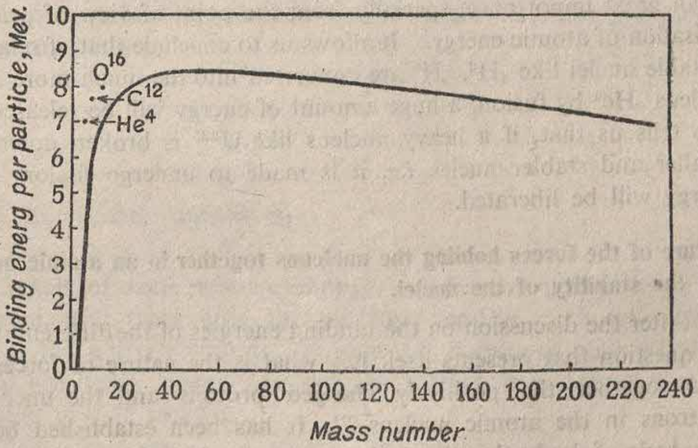


Fig. 4.1

A careful analysis of fig. 4.1, part by part, will reveal the following :

(a) At the beginning of the curve, *i.e.* in the case of nuclei with small mass numbers, the change in binding energy per nucleon is irregular. This is also apparent from the data in table 4.2.

(b) In the rather broad maximum of the curve, *i.e.* in the mass number region 40 to 120, the binding energy per nucleon is nearly constant, with a value around 8·5 Mev/nucleon.

(c) Nuclei with small mass numbers as well as those with large mass numbers have smaller binding energy per nucleon. Thus, these nuclei are less stable than the others and hence are suitable targets for bringing about *artificial transmutations**.

(d) After mass number 120, binding energy per nucleon gradually decreases from 8·5 Mev and comes down to 7·6 Mev per nucleon in uranium. This decrease in binding energy per nucleon is the real cause of the energy released when a heavy nucleus is broken down to smaller and stabler nuclei. In other words, *fission** is an energy-releasing or *exoergic* process in this mass region.

(e) From the first part of the curve, it is found that the binding energy per nucleon increases sharply in the mass region 1 to 20, and this increase continues at a much slower rate upto mass number 120. Hence, in this mass region, specially in the region 1 to 20 mass numbers, energy is released when the nuclei are formed by the addition of nucleons, *i.e. fusion** is an energy-releasing or *exoergic* process in this mass region.

Now we find that some of the above observations made from the the analysis of the binding energy curve of naturally occurring nucleides are of great importance, specially from the point of view of practical utilisation of atomic energy. It allows us to conclude that, if relatively unstable nuclei like ${}_1H^2$, ${}_2H^3$ are converted into the much more stable nucleus ${}_2He^4$ by fusion, a huge amount of energy will be released. It also tells us that, if a heavy nucleus like $U^{235}$ is broken down into smaller and stabler nuclei, *i.e.* it is made to undergo fission, much energy will be liberated.

### Nature of the forces holding the nucleons together in an atomic nucleus and the stability of the nuclei.

After the discussion on the binding energies of the different nuclei, the question that presents itself is, "what is the nature of forces that hold together the positively charged protons and the uncharged neutrons in the atomic nucleus ?" It has been established beyond any shade of doubt that the nuclear attractive forces are quite different from either gravitational force or electrostatic force with which we are familiar. It has also been established that three types of attractive forces exist within the nucleus. They are n – n, n – p and p – p-attractive forces. The most important characteristics of these nuclear attractive forces are :

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* These phenomena will be discussed in details later in this chapter.

1. All of these act over a **very short distance** of 2 f to 3 f (1 f = 1 Fermi = $10^{-15}$ cm.). Nuclear particles separated by a larger distance cannot attract each other.

2. These forces are **independent of the charges** on the interacting particles and the three forces are practically of equal magnitude.

3. All these forces show **saturation character.** Thus, a pair of nucleons involved in attractive interaction cannot attract other particles present nearby.

**The meson theory of nuclear binding forces.**

Like the two atoms held together by the mutual sharing of an electron-pair in a covalent molecule, a pair of nucleons may be held together by sharing a particle of appropriate mass and charge — this was the idea put forward by the Japanese physicist, H. Yukawa. Such a nuclear particle is called $\pi$-meson (see table 4.1). There are three types of $\pi$-mesons : positively charged $\pi^+$, negatively charged $\pi^-$ and neutral $\pi^\circ$ mesons. The attractive force between a neutron and a proton results due to an exchange of $\pi^+$ and $\pi^-$ mesons between them :

$$\begin{aligned} p^+ &\rightleftharpoons n + \pi^+, \\ n &\rightleftharpoons p^+ + \pi^- \end{aligned}$$

$\pi^\circ$ mesons bind two protons and two neutrons through the exchange processes :

$$p_1 \underset{\pi^\circ}{\overset{\pi^\circ}{\rightleftharpoons}} p_2$$

$$\text{and} \quad n_1 \underset{\pi^\circ}{\overset{\pi^\circ}{\rightleftharpoons}} n_2$$

As a result of such meson-exchanges, nuclear attractive forces are generated, and these hold the nucleons together with tremendous force in the nuclei of atoms. It must be mentioned that all these mesons are highly unstable outside the nucleus, having a life-time of the order of $10^{-6}$ seconds.

**Nuclear instability :** Apart from the attractive forces, coulombic repulsion between the like-charged protons also exists within the nucleus. The magnitude of the energy of coulombic repulsion between two protons at a distance of $3 \times 10^{-13}$ cm is approximately 0·5 Mev, which is much less than the average binding energy 8 Mev per nucleon. Inspite of its small magnitude, the coulombic repulsion becomes important because, unlike the nuclear attractive forces, it is neither of short-range nor of saturation character. It can act at a much longer distance and is proportional to the number of proton-pairs in the nucleus. Thus, it increases considerably with the increase in atomic number, Z. This is reflected in the decrease in the binding energy per nucleon in the case of the heavy elements. For a mass number greater than 200, this repulsive effect is so strong that those nuclei become unstable, and they spontaneously emit energetic particles whereby they get rid of their excess energy.

Thus, in an atomic nuclei there exist **cohesive forces** which bind the nucleons together and make the shape of the nucleus as spherical as possible, because a sphere is the solid figure which has the least surface area for a given volume and hence has the least energy. **Repulsive coulombic forces** tend to deform the nucleus, acting against the cohesive forces and make it energetically unstable. The contribution of repulsive forces increases at a rate faster than the attractive forces with the increase in mass number, and above the mass number 200, the nucleus gets considerably deformed and becomes susceptible to spontaneous disintegration.

### Liquid-drop model of the atomic nucleus.

The above situation is similar to that existing in a liquid drop being formed at the end of a small-bore tube hanging vertically downwards. The cohesive forces of surface tension keep the drop spherical against the force of gravity which tends to make it elongated. But, as the liquid drop grows larger, the force of gravitation predominates over the cohesive force of surface tension and elongates the drop. The nuclear attractive forces represent the surface tension forces, while the repulsive forces represent the gravitational forces acting on a liquid drop tending to deform it as it grows in mass. This is known as the **liquid-drop model** of the nucleus proposed by Bohr and Wheeler.

### The neutron-proton ratio in a neucleus and its implications.

Of the n—n, n—p and p—p attractive forces, the p—p force has its repulsive side in which every proton repels every other proton, and this extends throughout the nucleus. This tends to make the nucleus unstable. It can be overcome by the increase in the n—n and n—p attractive forces, which may be effected by increasing the number of neutrons at a faster rate than the number of protons. The addition of a neutron increases the attractive forces without increasing the repulsion. This actually happens in nature. Figure 4.2 represents the relation between the number of neutrons and protons in **stable** naturally occuring nuclei.

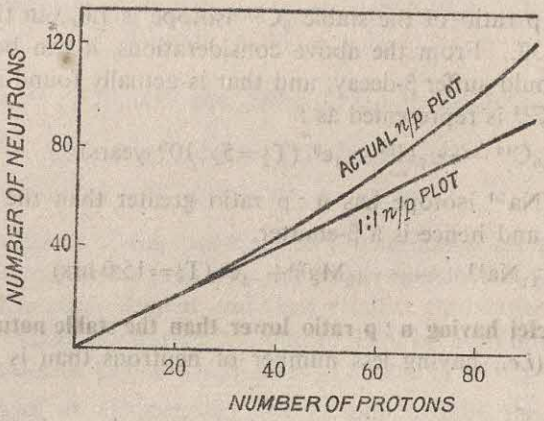


Fig. 4.2

For nuclei with atomic number up to 20, the n : p ratio is 1 : 1. The lower line in fig. 4.2 represents 1 : 1 n : p ratio. After atomic number 20, the n : p ratio increases above 1 : 1 and goes on increasing up to lead and bismuth (at. no. 82 and 83), where it becomes greater than 1.5. But, even this increase in the n : p ratio is not sufficient to compensate the fast growing p—p repulsion, as a result of which B.E./nucleon steadily decreases. For elements after bismuth, though the n : p ratio becomes 1.6, the repulsive force is of such magnitude that the nuclei undergo spontaneous disintegration.

**Prediction of the modes of decay.**

From the foregoing discussion, it is clear that the nuclei with higher or lower n : p ratio than is represented by the curve in fig. 4.2, will be unstable and exhibit spontaneous break-down or radioactivity. They will emit energetic particles which will help the resultant nuclei to attain the n : p ratio represented by the curve. Two different cases may be distinguished in such a process :

1. **For nuclei lying above the curve** (*i.e.* elements having more neutrons than is required for their stability) :

An isotope lying above the curve has more neutrons than that required for its stability. Hence, it will tend to decrease the number of neutrons which can be done either (i) by emitting one neutron or

(ii) by emitting a β-particle whereby a neutron is converted into a proton. Emission of neutron is a very rare process and the process (ii) is more efficient because, in one stroke it reduces the number of neutrons as well as increases the number of protons, and thereby reduces the n : p ratio to a greater extent.

The n : p ratio of the stable $_6C^{12}$ isotope is 1.0, but that of $_6C^{14}$ isotope is 1.33. From the above considerations, it can be predicted that $_6C^{14}$ should suffer β-decay, and that is actually found in practice. β-decay of $_6C^{14}$ is represented as :

$$_6C^{14} \longrightarrow {}_7N^{14} + {}_{-1}e^0 \quad (T_{\frac{1}{2}} = 5 \times 10^3 \text{ years}).$$

Similarly, $_{11}Na^{24}$ isotope has n : p ratio greater than the stable isotope $_{11}Na^{23}$ and hence is a β-emitter.

$$_{11}Na^{24} \longrightarrow {}_{12}Mg^{24} + {}_{-1}e^0 \quad (T_{\frac{1}{2}} = 15 \cdot 0 \text{ hrs})$$

2. **Nuclei having n : p ratio lower than the stable naturally occurring isotope** (*i.e.*, having less number of neutrons than is needed for stability) :

An isotope with less number of neutrons than what is required, will tend to increase it by converting one of its protons to a neutron (i) by emission of a positron or (ii) by capturing an orbital electron (K-electron capture). However, (i) is a more favourable process and generally occurs. $_{15}P^{30}$ has a n : p ratio less than its stable isotope $_{15}P^{31}$ and hence it should be radioactive and decay by positron emission :

$$_{15}P^{30} \longrightarrow {}_{14}Si^{30} + {}_{+1}e^0 \quad (T_{\frac{1}{2}} = 2 \cdot 55 \text{ minutes}).$$

For similar reasons, $_7N^{13}$ is a positron-emitter.

$$_7N^{13} \longrightarrow {}_6C^{13} + {}_{+1}e^0 \quad (T_{\frac{1}{2}} = 9 \cdot 9 \text{ minutes}).$$

Orbital-electron capture occurs in the case of neutron-deficient nuclei of comparatively high atomic number. An example is,

$$_{26}Fe^{55} + {}_{-1}e^0 \longrightarrow {}_{25}Mn^{55}.$$

This electron is captured from the orbital nearest to the nucleus, *i.e.* from K-level and hence is also known as **K-capture**. Since by such a process, a vacancy for an electron is created in the K-shell, an electron from the next higher level drops down to occupy the vacant position in the K-shell and X-rays of energy equal to the difference in energies of the K and L levels are emitted. In a similar manner, one electron drops from each successive energy level until the system is normalised and thereby forms a series of lines in the X-ray spectrum.

**Isotopes** : Isotopes are atoms of the same element containing the same number of protons but different number of neutrons in their nuclei. In other words, isotopes have same atomic number but different atomic masses. Since the isotopes have the same atomic number and hence the same electronic configuration, their chemical properties are the same. Examples of isotopes, both stable and radioactive, are numerous and some of them are given below :

$_{17}Cl^{35}$ and $_{17}Cl^{37}$ ; $_8O^{16}$, $_8O^{17}$ and $_8O^{18}$ ; $_6C^{12}$, $_6C^{13}$ and $_6\overset{*}{C}{}^{14}$

$_{15}P^{31}$ and $_{15}\overset{*}{P}{}^{32}$ ; $_1H^1$, $_1H^2$ and $_1\overset{*}{H}{}^3$ ; $_{92}\overset{*}{U}{}^{235}$ and $_{92}\overset{*}{U}{}^{238}$

The isotopes marked with asterix are radioactive.

The deviations of the experimentally determined atomic weights from whole-numbers are primarily due to the existence of the different isotopes of the same element and their relative abundance in nature. The atomic weight of chlorine is found to 35·5, because in nature, two isotopes of chlorine $Cl^{35}$ and $Cl^{37}$ exist in a ratio of 75·4% to 24·6%.

Isotopes of an element can also be obtained by the process of artificial transmutation :

$$_{11}Na^{23} + {_1H^2} \longrightarrow {_{11}Na^{24}} + {_1H^1}$$

$$_{19}K^{39} + {_0n^1} \longrightarrow {_{19}K^{38}} + 2{_0n^1}$$

All (n, γ) reactions produce isotopes of the target element.

**Isobars** : Isobars are atoms having the same mass number (total number of protons and neutrons) but different numbers of protons, *i.e.*, they are atoms of different elements having different atomic numbers but the same mass number. Since their atomic numbers are different, they differ in chemical and physical properties. Some examples of isobars are : $_{18}Ar^{40}$ and $_{20}Ca^{40}$ ; [illegible], [illegible] and [illegible]; [illegible] and [illegible] ; [illegible] and [illegible].

A radio-nucleide may be converted into its isobar by (i) positron emission, (ii) $\beta^-$ emission and also by (iii) orbital electron capture.

$$_{15}P^{30} \longrightarrow {_{14}Si^{30}} + {_{+1}e^0} \; ; \; {_{11}Na^{24}} \longrightarrow {_{12}Mg^{24}} + {_{-1}e^0}$$

[illegible] $+ {_{-1}e^0} \longrightarrow$ [illegible] (orbital electron capture)

**Isotones** : These are atoms containing the same number of neutrons but with different mass numbers. In other words, they are atoms of different elements containing same number of neutrons. Thus, unlike the isotopes, where the variable factor in the nucleus is the number of neutrons, the number of protons is the variable in the case of isotones. Hence, isotones have different physical and chemical properties. A few examples of isotones are given below :

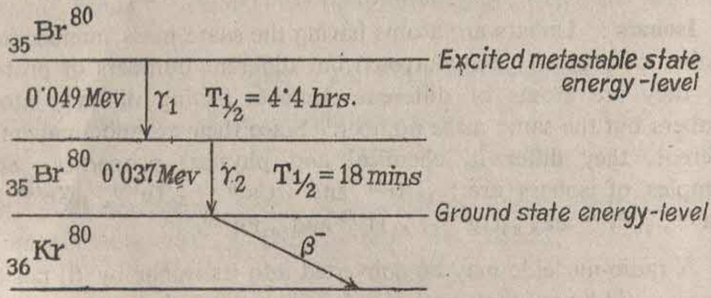
$_{88}Ra^{226}$ and $_{89}Ac^{227}$ ; $_{14}Si^{30}$, $_{15}P^{31}$ and $_{16}S^{32}$.
(138 neutrons) (16 neutrons)

**Nuclear isomers :** Nuclear isomers are the atoms of the same element with the same mass number, and they differ from each other only in their radioactive properties which are manifested through the emission of γ-rays. Such a decay of one nuclear isomer to the other through the emission of γ-rays is known as *isomeric transition.* Such isomers are also known as **isobaric isotopes.** More than 130 cases of nuclear isomerism are known at present. A good example is found in the case of $_{35}Br^{80}$.

When $_{35}Br^{79}$ is irradiated with neutrons, it forms $_{35}Br^{80}$ according to the nuclear reaction,

$$_{35}Br^{79} + {}_0n^1 \longrightarrow {}_{35}\overset{*}{Br}{}^{80}.$$

Freshly formed $_{35}\overset{*}{Br}{}^{80}$ exists in a high-energy metastable state. It emits two γ-rays of different energies, one after the other, and reaches the ground state, which then emits a β-particle to form $_{36}Kr^{80}$. This is represented in the diagram below :



**Principles of separation of isotopes.**

Though isotopes have identical electronic configurations, extremely small differences in their chemical properties are observed due to the difference in the so-called **zero point energy** for the bonds involving the two isotopic species. This is the reason for the slight differences in the chemical reactivity and physical properties between two isotopic molecules like $H_2O$ and $D_2O$. Due to the small difference in mass, the difference in physical properties of the isotopes are also small, and are more pronounced in the case of lighter isotopes, where the *percentage difference of mass* is high. However, by converting the isotopes into suitable compounds, and magnifying the difference of one property by means of external agencies or devices like the application of electric or magnetic field, applied pressure *etc*., an isotopic combination may be sufficiently enriched with respect to one isotope.

The extent of enrichment of an isotope, in a mixture of two, is given by the separation factor ($S$) of the process, which is given by the expression,

$$S = \frac{n_1'/n_2'}{n_1/n_2},$$

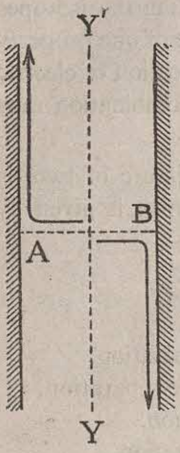
where $n_1$ = no. of atoms of the light isotope before separation,
$n_2$ = " atoms of the heavier isotope before separation,
$n_1'$ = " atoms of light isotope after separation,
$n_2'$ = " atoms of heavier isotope after separation.

A large number of methods are used for the enrichment of isotopes, and the underlying principles of a few most important methods will be briefly discussed.

**Gaseous diffusion method** : According to Graham's law, the rate of diffusion of a gas is inversely proportional to the square-root of its molecular weight. Thus, when a mixture of two isotopes (either in the elemental form or as a volatile compound) is allowed to pass through a porous barrier, preferably into a vacuum, the gas accumulating in the low-pressure area will get enriched in the lighter isotope. This enriched gas is now subjected to a similar separation step, when it is further enriched in the lighter isotope. The number of such steps may be increased so as to get the desired enrichment. During the second World War, $U^{235}$ and $U^{238}$ isotopes were separated for atomic bomb preparation employing this method, by using the volatile hexafluorides ($UF_6{}^{235}$ and $UF_6{}^{238}$).

**Thermal diffusion method** : When a gaseous mixture of a light and a heavy isotope (either in the elemental state or as a volatile compound) is kept within a space between two surfaces at different temperatures, the light molecules tend to diffuse to the high temperature region, while the heavy molecules move towards the lower temperature area. The principle of the method is shown in fig. 4.3.

If a gaseous mixture of two isotopes are placed between two vertical plates, the lighter molecules will be concentrated near the hot plate and the heavier will get accumulated at the cold plate. At the same time, convection currents will help the lighter molecules to move up and the heavier ones to settle down. The resultant effect of the setting up of a concentration gradient along AB and along YY′ is the transportation of the lighter isotope towards the top, while the heavier isotope gets concentrated at the bottom. Using several such coloumns and allowing sufficient time intervals, 99·6% enrichment of $Cl^{35}$-isotope from a natural mixture of $Cl^{37}$ and $Cl^{35}$ was obtained by this method, using HCl gas as the material.



A is the hotter plate and B is the colder one.

Fig. 4.3

**Method of electrolysis** : This method is based on the difference in the rate of electrolysis of ${}_1H^1{}_2O$ (ordinary water) and ${}_1H^2{}_2O$ (heavy water) from an alkaline solution, 0.5N with respect to NaOH. As the electrolysis is started, ${}_1H^1{}_2O$ suffers electrolysis at a higher rate than ${}_1H^2{}_2O$ and hence ${}_1H^2{}_2O$ accumulates in the residual water in the cell. The concentration of NaOH is kept constant by removing excess NaOH by passing $CO_2$, or by adding NaOH from outside if it falls short. Starting with a volume of 2311 litres of water, 99% ${}_1H^2{}_2O$ is obtained when the volume of the residual solution in the electrolytic cell comes down to 82 ml.

**Evaporation method** : This method is based on the principle that the rate of evaporation of the molecules (or atoms) from a mixture of isotopes (or their volatile compounds) is inversely proportional to the square-root of their masses, and is similar to the method of enrichment by diffusion method. If the mixture of the two isotopes are allowed to evaporate from a surface into vacuum, the lighter isotope will leave the surface at a faster rate than the heavier isotope. Now, if the evaporated molecules are immediately condensed on some other surface previously cooled below its temperature of condensation, the condensed liquid will be enriched in the lighter isotope. This condensate can again be subjected to a similar separation step and can be further enriched. Isotopes of mercury were partially separated by this method.

**Electromagnetic method** : An isotopic mixture, converted into positive ions in a discharge tube, is accelerated by passing through an electric field and then led into a powerful magnetic field perpendicular to the direction of the electric field. This magnetic field bends the ion-beam and, depending on their charge/mass (e/m) ratio, the charged particles are focussed to different points, and isotopes of different masses can be completely separated. This principle is shown diagramatically in Fig. 4.4.

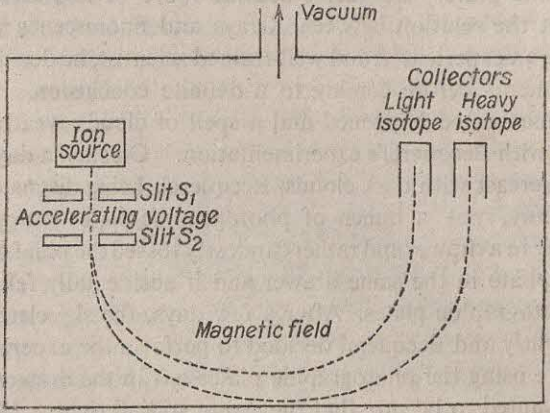


Fig. 4.4

This principle was utilised in the different mass spectrographs devised by Aston, Bainbridge and others. Separation of $U^{235}$ and $U^{238}$ during World War II was achieved by this method.

**Discovery of radioactivity.**—In Chapter I, we have mentioned that the phenomenon of radioactivity was discovered in 1896 by the French physicist, Henry Becquerel. It was an attempt by Becquerel to show that fluorescent substances emit X-rays that resulted in the discovery of the phenomenon of radioactivity. Fluorescent substances, on exposure to a source of radiation, absorb energy from it and start emitting the stored energy in the form of radiations of wavelength different from that of the source. However, the emitted radiation stops immediately when the source of excitation is cut off. It may be noted here that Becquerel was extremely fortunate in that, the fluorescent substance he used was a sample of pure **potassium uranyl sulphate** which he inherited from his father. An observation was made by H. Poincare that a green fluorescence is produced at the point of the X-ray tube through which the X-rays emerged out. Becquerel thought, if X-rays can cause fluorescence, it may be true that a fluorescent substance emits X-rays. To test the correctness of his idea, he put a small phial containing the fluorescent uranium salt on a photographic plate wrapped in thick black paper (to prevent the plate from being affected by sunlight), and put the assembly in bright sunlight for a definite period of time in order to activate the uranium compound to produce fluorescence. The photographic plate, on developing, exhibited a clear image of the phial, which indicated that the fluorescent substance emitted X-ray-like radiations that passed through the thick black paper and affected the photographic plate. Becquerel became more or less certain that his idea about the relation between X-rays and fluorescence was correct. Still, being an experienced and well-trained scientist, he decided to repeat his experiments before coming to a definite conclusion. It was then that the unexpected happened and a spell of cloudy weather seriously interfered with Becquerel's experimentation. On such a day, when the sky was overcast with dark clouds, Becquerel, being disgusted with the sunless hours, put a bunch of photographic plates wrapped in thick black paper in a drawer and rather carelessly tossed the phial of patassium uranyl sulphate in the same drawer and it accidentally fell on the top of the photographic plates. After a few days, the sky cleared, the sun shone brightly and Becquerel decided to perform the experiment again. But, before using the photographic plates left in the drawer for several days, he wanted to be sure that they were still all right. He developed the top one from the bunch. To his utter surprise, he found a clear image of the phial on that plate, which was much more strong than the image obtained in presence of sunlight ! Becquerel was baffled ! Since the uranium salt was not exposed to sunlight, it could not emit fluorescent radiations and hence cannot affect the photographic plate. He repeated the experiment several times in total darkness and obtained identical results. He performed experiments with other uranium compounds and observed similar effect. Then he was forced to abandon his hypothesis of fluorescence causing the generation of X-rays and had to conclude that the sample itself was active in its own peculiar way and did not require the help of sunlight to activate it. Thus, ultimately Becquerel reached the conclusion that, uranium compounds have the unusual property of spontaneously emitting peculiarly penetrating radiations resembling X-rays. The name **radioactivity** was given to this previously unknown and totally new phenomenon by Mme. Curie.

Soon after the discovery of radioactivity, Mme. Curie and her husband, Pierre Curie, discovered two new elements from the uranium ore, pitchblende, which showed similar phenomenon of radioactivity. They were named radium (Ra) and polonium (Po), and both of them were far more active than uranium. In 1903, Becquerel, along with Mme. Curie and Pierre Curie, received Nobel prize in physics as a recognition of their revolutionary work on radioactivity. The elements exhibiting radioactivity were called **radioactive elements** or simply **radio elements** or radio nucleides.

**The nature of the radiations emitted by radio elements : $\alpha$, $\beta$ and $\gamma$-rays.**

The discovery of the phenomenon of radioactivity by Becquerel and the poineering works by the Curies as well as the group of workers headed by Rutherford, inspired scientists of all developed countries. In no time, a wealth of informations covering various aspects of radioactivity accumulated. As time went on, more and more scientists got involved in this line of research. We have already mentioned in the first chapter that the radioactive radiations, emitted by substances such as uranium, can be separated into three distinct varieties by the action of either magnetic or electric field (see fig. 1.6). The $\alpha$-particles, being positively charged, are deviated towards the negatively charged plate and the $\beta$-rays bend towards the positively charged plate due to their negative character, while the $\gamma$-rays pass undeviated, because they are electromagnetic waves of very short wave-length. The more important properties of the three kinds of radiation are given below in Table 4.3.

TABLE 4.3

| Property | $\alpha$-rays | $\beta$-rays | $\gamma$-rays |
|---|---|---|---|
| Nature. | These are doubly charged helium nuclei denoted by $He^{+2}$ and are deflected towards the $-$ve plate of the electric field. | These are fast-moving electrons and are denoted by e, $e^-$, $_{-1}e^\circ$ *etc.* They are deflected towards the positive electrode. | $\gamma$-rays are electromagnetic radiations of wavelength even shorter than the X-rays ($10^{-8}$–$10^{-11}$ cm). They are not deflected in the electric field. |
| Velocity. | The velocity of the $\alpha$-particles lies in the range $1{\cdot}4\times10^9$ to $1{\cdot}7\times10^9$ cms/sec. and it depends on the radioactive substance which emits them. | The velocity of the $\beta$-particles ranges from $\frac{1}{10}$th to $\frac{9}{10}$th of the velocity of light and it depends upon the radio element from which they are emitted. | The $\gamma$-rays possess the same velocity as that of light, *i.e.* $3\times10^{10}$ cms./sec. |
| Ionization of air or other gases. | On collision with the gas molecules in air, the $\alpha$-rays knock off electrons and produce intense ion- | $\beta$-particles also cause ionization in air, but as its kinetic energy is much less than the $\alpha$-particles, | The ionization produced by $\gamma$-rays is small and is 10,000 times smaller than that produced by |

TABLE 4.3—*Contd.*

| Property | $\alpha$-rays | $\beta$-rays | $\gamma$-rays |
|---|---|---|---|
| | ization. Compared to the $\beta$-particles, the ionizing power of the $\alpha$-particles is 100 times greater. | its ionizing capacity is 100 times less than that of the $\alpha$-particles. | the $\alpha$-particles. |
| Penetrating power. | $\alpha$-particles, being bulkier and comparatively slower, have least penetrating power of the three, and are stopped by a 0·1 mm. thick aluminium foil. | $\beta$-particles, being smaller and faster, are much more penetrating than the $\alpha$-particles and are stopped by an aluminium foil of 5 mm. thickness. It is almost 50 times more penetrating than $\alpha$-particles. | They are very highly penetrating, even more penetrating than X-rays. They can pass through thick sheets of aluminium and steel and are stopped by lead blocks of a few cm. thickness. |
| Physiological action. | When exposed to $\alpha$-rays, the body suffers severe burns, but it is only skin-deep due to their small penetrating power. | Physiological actions of the $\beta$-particles are not much pronounced. | The $\gamma$-rays are very harmful to living cells. In high doses, it can cause malignancy. However, as it preferentially attacks malignant cells, in well-regulated doses it is used for the cure of cancer. This is called radiotherapy. |

**Theory of radioactive disintegration.**

Detailed and careful studies of the radio elements like uranium and thorium by workers like Crooks, Rutherford and Soddy revealed certain new and interesting facts, which helped to get a deeper insight into the phenomenon of radioactivity and its implications to chemistry of elements in general.

It was noticed that, if ammonium carbonate is gradually added to an aqueous solution of thorium nitrate, $Th(NO_3)_4$, a precipitate was formed at first, which practically dissolved on addition of an excess of the reagent, leaving a very small amount of a flocculent precipitate. This is filtered off and the minute residue was found to be highly active.

But, the major residue, obtained by the evaporation of the solution, showed very feeble activity. The active substance did not dissolve in excess ammonium carbonate and hence was chemically different from thorium. It was named thorium X (ThX). It was then observed that within a few days, the ThX was losing its activity, while the major residue of Th, free from ThX, gradually regained its activity at a rate equal to that at which ThX was losing its activity. The rate of decay of ThX and the rate of recovery of the activity of Th is shown in Fig. 4.5

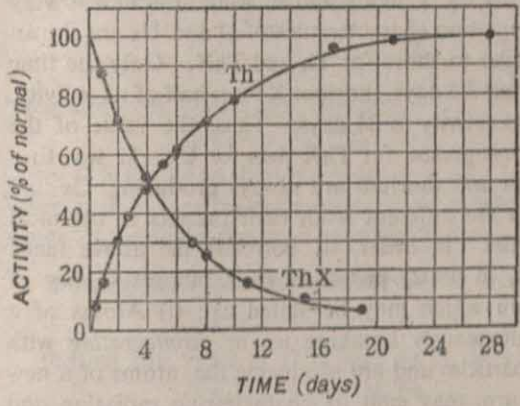


Fig. 4.5

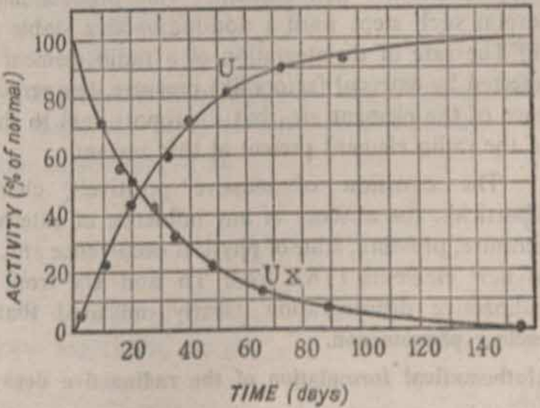


Fig. 4.6

From the above figure 4.5, it is apparent that the experimental decay curve of ThX is exponential in character and hence the activity can be expressed as a function of time by the equation, $A_t = A_0 e^{-\lambda t}$ ...(4.1) where $A_0$ is the initial activity of ThX, $A_t$ is the activity after a time $t$ and $\lambda$ is a constant, called the **disintegration constant.** The curve representing the recovery of the activity of Th is found to obey the equation : $A_t' = A_o' (1 - e)^{-\lambda t}$ .. .. (4.2) where $A_o'$ is the initial activity of Th at the beginning and $A_t'$ represents its activity after a time t and $\lambda$ is the same constant as in equation (4.1).

A parallelism is found in the case of uranium which, on disintegration, gave rise to a new substance Ux, chemically different from the parent uranium. This Ux is highly active, while uranium is very feebly active. The disintegration characteristics of U and Ux are shown in figure 4.6 and is similar to those for Th and ThX. Only the time scale is different. In about 3.5 days, thorium X loses half of its activity, while Ux loses half of its activity in 24 days. Thus, the value of the disintegration constant $\lambda$ is greater for ThX than for Ux. It was thus established that uranium and thorium are always producing Ux and ThX respectively, which are different from their parents in chemical and radioactive properties. In order to correlate the above facts, Rutherford and Soddy, in 1902, proposed their famous theory of radioactive disintegration which may be stated as : (i) Atoms of a radio element are spontaneously breaking up or *disintegrating* with the emission of $\alpha$ or $\beta$ particles and are producing the atoms of a new element which, in its turn, may emit its characteristic radiation and produce another new element. This process may proceed through several such steps until a non-radioactive stable nucleide is formed, (ii) The rate of disintegration of a radio element at any time is not affected by external factors like pressure, temperature, state of occurrence of the element *etc.*, but is proportional to the number of atoms of the radio element present at that instant.

The emission of massive positively charged particles like $\alpha$-particles, the absence of any influence of external factors like temperature, pressure, state of physical occurrence *etc.*, and the production of new elements (ThX from Th and Ux from U) as a result of radioactive disintegration, clearly indicated that **radioactivity is a nuclear phenomenon.**

### Mathematical formulation of the radioactive decay process.

If N represents the number of atoms of a radio element present at a time t, and if dN number of atoms decay in a very small interval of time dt, then $\frac{dN}{dt}$ represents the rate of decay of the radio element in question. Now, according to the theory of radioactive disintegration, this is proportional to number of atoms present at that time, *i.e.*

$$\text{Rate of decay, } -\frac{dN}{dt} \propto N; \text{ or, } -\frac{dN}{dt}=\lambda N \qquad \ldots \qquad \ldots (4.3)$$

where $\lambda$, the disintegration constant, is a specific property of a radio element. No two different radio elements can have the same disintegration constant. The negative sign indicates that the number of atoms of the radio element is always diminishing. This first order differential equation (4.3) has to be integrated before it can be put to any practical use. The equation (4.3) can be rearranged as,

$$\frac{dN}{N} = -\lambda dt.$$

Integrating the above eqn., we get,

$$\log_e N = -\lambda t + C \qquad \ldots \qquad \ldots \qquad \ldots (4.4)$$

where C is the integration constant.
When $t=0$ (*i.e.* at the beginning), $N=N_0$, where $N_0$ is the number of atoms of the radio element at the beginning.

Putting these boundary conditions in eqn. (4.4), we get,

$$\log_e N_0 = -\lambda \times o + C; \text{ or, } C=\log_e N_0.$$

Putting this value of C in eqn. (4.4), we get,

$$\log_e N = -\lambda t + \log_e N_0$$

$$\text{or, } \log_e \frac{N}{N_0} = -\lambda t \qquad \ldots \qquad \ldots \qquad \ldots (4.5)$$

$$\text{or, } N=N_0 e^{-\lambda t} \qquad \ldots \qquad \ldots \qquad \ldots (4.6)$$

This equation is another form of eqn. 4.5 and represents the exponential nature of the decay curve obtained experimentally.

The eqn. (4.5) can be rearranged as,

$$\log_e \frac{N_0}{N} = \lambda t \qquad \ldots \qquad \ldots \qquad \ldots (4.7)$$

$$\text{or, } \lambda = \frac{1}{t} \log_e \frac{N_0}{N} \qquad \ldots \qquad \ldots \qquad \ldots (4.8)$$

Converting to common logarithm, we get,

$$\lambda = \frac{2{\cdot}303}{t} \log \frac{N_0}{N} \qquad \ldots \qquad \ldots \qquad \ldots (4.9)$$

Thus, radioactive decay is a **first order process** and the decay constant has the dimension of $(\text{time})^{-1}$. It can be used to calculate the decay constant of a radio element.

**Half-life of a radio element.**

The half-life of a radio element ($T_{\frac{1}{2}}$) is **the time in which half of the atoms of the radio element will disintegrate.**

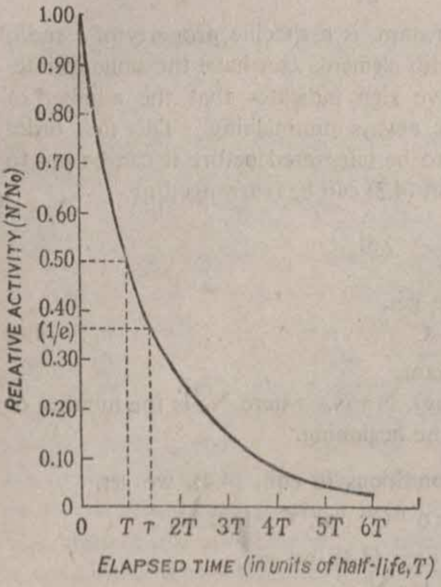


Fig. 4.7

The relationship between the activity and the half-life is illustrated in figure 4.7.

After *n* half-lives ($t = nT_{\frac{1}{2}}$), the fraction of the activity remaining is $(\frac{1}{2})^n$. This fraction becomes very small, but it never becomes zero. After 6 half-lives it is $\frac{1}{64}$ and after 8 half-lives it becomes $\frac{1}{256}$ and after 10 half-lives it reduces to $\frac{1}{1024}$ of its initial activity.

The eqn. (4.9) can be rearranged as,

$$t = \frac{2{\cdot}303}{\lambda} \log \frac{N_0}{N} \quad .. \quad (4.10)$$

To find an expression for the half-life period, we have to find out the time $T_{\frac{1}{2}}$, in which the number of atoms N left behind, becomes equal to $\frac{N_0}{2}$, where $N_0$ is the number of atoms in the beginning. Thus, the expression for half-life of a radio element can be obtained from eqn. (4.10) by putting $N = \frac{N_0}{2}$. So, $T_{\frac{1}{2}} = \frac{2{\cdot}303}{\lambda} \log \frac{N_0}{\frac{N_0}{2}}$

$$\text{or, } T_{\frac{1}{2}} = \frac{2{\cdot}303}{\lambda} \log 2 \text{ ; or, } T_{\frac{1}{2}} = \frac{2{\cdot}3030}{\lambda} \times 0{\cdot}3010.$$

$$\text{Hence, } T_{\frac{1}{2}} = \frac{0{\cdot}6931}{\lambda} \quad .. \quad .. \quad .. \quad (4.11)$$

The eqn. 4.11 shows that, like a true first order process, the half-life of a radio element is independent of the number of atoms present initially.

Since $\lambda$ is a specific property of a radio element, $T_{\frac{1}{2}}$ is also its characteristic property and no two elements can have equal half-lives. Thus, half-life of radio elements can be obtained if the disintegration constant is known and vice-versa.

Now let us consider a problem in the light of our knowledge acquired upto the present.

(a) In what time 1 gm. of radium will become 0·01 gms., if its half-life is 1590 years ?

We know that, $\lambda = \frac{0{\cdot}693}{T_{\frac{1}{2}}} = \frac{0{\cdot}693}{1590}$ years$^{-1}$

Let $t$ be the time required for 1 gm. of radium to become 0·01 gm. From the conditions of the problem, $N_0 = \frac{1 \times 6{\cdot}02 \times 10^{23}}{\text{At. wt. of Ra}}$

$$\text{and } N = \frac{0{\cdot}01 \times 6{\cdot}02 \times 10^{23}}{\text{At. wt. of Ra}}$$

are the atoms of Ra present initially and after time $t$. Here $\frac{N_0}{N} = 100$.

Now, from eqn. (4.9), $\frac{2{\cdot}303}{\lambda} \log \frac{N_0}{N} = t$

Or, $t = \frac{2{\cdot}303 \times 2 \times 1590}{0{\cdot}693} = 10567$ years.

**Average life of a radio element.**

From the exponential nature of the decay curves, it is clear that the activity of a radio element becomes zero only after an infinite time, though the atoms are constantly disintegrating. It means that, any atom of a radio element can disintegrate just now, or an infinite time may elapse before it disintegrates. So, every individual atom can have different lives ranging from zero to infinity. The average life of a radio element is given by,

$$\frac{\text{The sum of the lives of all the atoms}}{\text{Total number of atoms.}}$$

Let us consider N number of atoms of a pure radio element separated from its own disintegration products at time $t$, and assume that dN number of these atoms disintegrate in the time interval between $t$ and $t + dt$. N being the number of atoms actually present, we have, $\frac{dN}{dt} = -\lambda N$, or $-dN = N\lambda dt$ .. .. (4.12)

Putting $N = N_0 e^{-\lambda t}$ in the above eqn. (4.12),

we have, $-dN = \lambda N_0 e^{-\lambda t} dt$, .. .. (4.13)

where $N_0$ is the number of atoms at the time, $t = 0$.

Each of these dN number of atoms will disintegrate between the time *t* and t+dt. Since dt is very small, these dN atoms may be taken to have a life of t seconds.

Thus, the total life of $-dN$ number of atoms $= -tdN$

Since the possible life of any of the total number of atoms may vary from zero to infinity, the total life of all the $N_0$ atoms is given by,

$$\int_0^\alpha -tdN. \quad \therefore \quad \text{Average life } (\tau)=\frac{\int_0^\alpha -tdN}{N_0}=\frac{1}{N_0}\int_0^\alpha -tdN \quad .. \quad (4.14)$$

Putting the value of $-dN$ from eqn. 4.13,

$$\text{we have, } \tau=\frac{1}{N_0}\int_0^\alpha \lambda\, N_0 e^{-\lambda t}\, tdt$$

$$=\lambda\int_0^\alpha e^{-\lambda t}\, tdt$$

$$=\lambda\left[\frac{e^{-\lambda t}}{-\lambda}t-\int\frac{e^{-\lambda t}}{-\lambda}dt\right]_0^\alpha$$

$$=\lambda\left[\frac{e^{-\lambda t}}{-\lambda}t-\frac{e^{-\lambda t}}{\lambda^2}\right]_0^\alpha$$

$$=-\frac{1}{\lambda}\left[(\lambda t+1)e^{-\lambda t}\right]_0^\alpha$$

$$\therefore \quad \tau=\frac{1}{\lambda} \quad .. \quad .. \quad .. \quad (4.15)$$

Thus, the **average life** or **mean life** ($\tau$) of a radio element is the reciprocal of its disintegration constant and it can be easily calculated if $\lambda$ is known.

We have already known that,

$$T_{\frac{1}{2}}=\frac{0{\cdot}6931}{\lambda}. \quad \therefore \quad \frac{T_{\frac{1}{2}}}{\tau}=0{\cdot}6931, \text{ or } T_{\frac{1}{2}}=0{\cdot}6931\,\tau \quad .. \quad (4.16)$$

Thus, knowing any one of $T_{\frac{1}{2}}$ or $\tau$, the value of the other can be calculated.

**Units of radioactivity.**

Like all other quantitative measurements, the measurement of radioactivity naturally needs some units to be defined. The primary unit used for measuring radioactivity is "**disintegrations per second**" or dps. Since the disintegrations per second are generally very large numbers, this has been replaced by the unit **curie (c)**. By **one**

**curie** we mean **an amount of the radioactive material which decays at a rate of** $3{\cdot}7\times10^{10}$ dps. A *millicurie* (*mc.*) is $1\times10^{-3}$ curie and $1\times10^{-6}$ curie is called a *microcurie* (μc).

Another unit of radioactivity is the **rutherford** (*rd*). It is defined as the amount of radioactive material which gives $10^6$ dps. Thus, one *millirutherford* (*mrd*) and one *microrutherford* (μ*rd*) correspond to $10^3$ dps and 1 dps respectively.

**Problem :** Calculate the weight in gms. of 10 curie and 10 rutherford of RaB ($Pb^{214}$) isotope, given its half-life to be 26·8 minutes.

We know that, $\lambda=\dfrac{0{\cdot}693}{T_{\frac{1}{2}}}=\dfrac{0{\cdot}693}{26{\cdot}8\times60}=4{\cdot}31\times10^{-4}\ \text{sec}^{-1}$.

Let W represent the required weight.

Since W is the weight in gms. of $Pb^{214}$, the number of atoms present in it is $\dfrac{W}{214}\times6{\cdot}02\times10^{23}=N$. Rate of decay, $-\dfrac{dN}{dt}=\lambda N$ (from eqn. 4.3)

$$=\frac{4{\cdot}31\times10^{-4}\times W\times6{\cdot}02\times10^{23}}{214}$$

$$=1{\cdot}21\ W\times10^{18}\ \text{dps.}$$

If $-\dfrac{dN}{dt}=10\times3{\cdot}7\times10^{10}$ dps (10 curies), then, $10\times3{\cdot}7\times10^{10}=1{\cdot}21W\times10^{18}$,

$$\text{or, } W=\frac{10\times3{\cdot}7\times10^{10}}{1{\cdot}21\times10^{18}}\ \text{gms.}=3{\cdot}1\times10^{-7}\ \text{gms.}$$

Similarly, for 10 rd, $W=\dfrac{10\times10^{6}}{1{\cdot}21\times10^{13}}=8{\cdot}3\times10^{-7}$ gms.

The theory of radioactive disintegration has told us that a radio element A emits characteristic radiations and forms a new element B. A is called the *parent* and B is named the *daughter* element. If B is radioactive, it will emit its own characteristic radiation and form another new element C, and the process will proceed in this manner until a stable (non-radioactive) end-product is reached. Such a series of radioelements is said to form a **radioactive disintegration series** in which each individual member, excepting the first one, is produced as a result of decay of the member just preceding it. Three such series of radio elements are found in nature and are called the **uranium series, the thorium series and the actinium series.** The first two series are named after their precurssors or the first members. It has been found that all these three disintegration series end with a stable isotope of lead. The **thorium series** is shown in Table 4.4. Thorium-232 ultimately decays to lead-208 which is stable and non-radioactive.

TABLE 4.4

| Radioactive species | Nucleide | Type of disintegration | Half-life | Disintegration constant (Sec$^{-1}$) |
|---|---|---|---|---|
| Thorium (Th) | $_{90}Th^{232}$ | α | $1{\cdot}39 \times 10^{10}$y | $1{\cdot}58 \times 10^{-18}$ |
| Mesothorium 1(MsTh1) | $_{88}Ra^{228}$ | β | 6·7 y | $3{\cdot}28 \times 10^{-9}$ |
| Mesothorium 2(MsTh2) | $_{89}Ac^{228}$ | β | 6·13 h | $3{\cdot}14 \times 10^{-5}$ |
| Radiothorium (RdTh) | $_{90}Th^{228}$ | α | 1·910 y | $1{\cdot}15 \times 10^{-8}$ |
| Thorium X(ThX) | $_{88}Ra^{224}$ | α | 3·64 d | $2{\cdot}20 \times 10^{-6}$ |
| Thorium Emanation (Tn) | $_{86}Tn^{220}$ | α | 51·5 s | $1{\cdot}34 \times 10^{-2}$ |
| Thorium A (ThA) | $_{84}Po^{216}$ | α, β | 0·16 s | 4·33 |
| Thorium B (ThB) | $_{82}Pb^{212}$ | β | 10·6 h | $1{\cdot}82 \times 10^{-5}$ |
| Astatine (At) | $_{85}At^{216}$ | α | $3 \times 10^{-4}$ s | $2{\cdot}3 \times 10^{-3}$ |
| Thorium C (ThC) | $_{83}Bi^{212}$ | α, β | 60·5 m | $1{\cdot}91 \times 10^{-4}$ |
| Thorium C′(ThC′) | $_{84}Po^{212}$ | α | $3{\cdot}0 \times 10^{-7}$s | $2{\cdot}31 \times 10^{6}$ |
| Thorium C″(ThC″) | $_{81}Tl^{208}$ | β | 3·10 m | $3{\cdot}7 \times 10^{-3}$ |
| Thorium D (ThD) | $_{82}Pb^{208}$ | Stable | | |

The Thorium Series

From beginning to end, this series involves six α- and five β-emissions, and there are twelve members in the series. We know that the atomic number of thorium is 90 and that of lead is 82. Thus, altogether a maximum of seven elements can be accommodated in the periodic table in the seven places in-between thorium and lead. Since we have got twelve members in the series, the problem of accommodating the 12 members in the nine available places of the periodic table posed a serious problem. Similar problems were also faced in the cases of other two disintegration series. At such a time, Soddy came forward with his famous **group displacement law** and solved the problem. The group displacement law is stated thus : "On emission of an α-particle, an element is displaced two places to the left of its present position in the periodic table. The emission of a β-particle shifts the product to one place to the right." Since the atomic number of an element is its ordinal position in the periodic table, the displacement law implies that, an α-particle emission decreases the atomic number of the product by two units and its mass is reduced by four units. The emission of a β-particle leaves the mass practically unchanged, while the atomic number is increased by one unit. If we keep in mind that an α-particle is a doubly charged helium nucleus, having a mass of four units and a charge of two units, and a β-particle is a fast-moving electron having one unit negative charge but negligible mass, the significance of the group displacement law becomes clear. Since the emission of a β-particle is preceded by the process $n \rightarrow p^+ + \beta$, the net result of a β-emission is an increase of one atomic number of the daughter element.

On the basis of the above law, it has been possible to accommodate all the members of the different disintegration series in the fewer available spaces of the periodic table. The arrangement of the thorium series is shown in fig. 4.8.

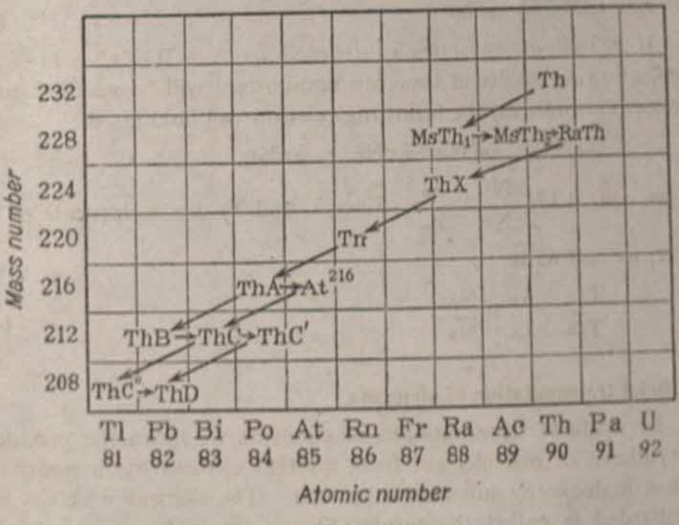


Fig. 4.8

It is to be noted that, if an element emits an α-particle and follows it up with two successive β-emissions, the element returns to its original position in the periodic table. Two such genetically related atoms, differing only in mass but having the same atomic number, are called **isotopes.** Though we have discussed about the *isotopes* earlier, the idea about them actually originated from the study of radioactivity.

**Radioactive Equilibrium.**

When a radioactive material stands over a long period of time, a condition known as *radioactive equilibrium* is established. (This actually happens when there is a radioactive series.) Such an equilibrium results from the fact that a series of radioactive elements are formed successively from a long-lived parent, and after a sufficient length of time, each element in the series is formed at the same rate as that of its decay. A radio element (A) decays into its daughter (B) which, if radioactive, decays into its daughter (C). Let $\lambda_A$ and $\lambda_B$ represent the disintegration constants of (A) and (B). Then the rate of decay of (A) and (B) will be represented at $-\frac{dN_A}{dt} = \lambda_A N_A$ and $-\frac{dN_B}{dt} = \lambda_B N_B$ respectively, where $N_A$ and $N_B$ are the number of atoms of (A) and (B). Under the conditions of radioactive equilibrium, the rate of disintegration of (A) will be equal to that of (B), *i.e.*, $\lambda_A N_A = \lambda_B N_B$. .. .. .. (4.17)

If a radioactive series is denoted as $A \rightarrow B \rightarrow C \rightarrow D \rightarrow$ ..... then, allowing sufficient time, an equilibrium will be reached, and in these circumstances, the following relation will hold good :

$$\lambda_A N_A = \lambda_B N_B = \lambda_C N_C = \lambda_D N_D \qquad (4.18)$$

From eqn. 4.17, $\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A}$. Since $\lambda$ and $T_{\frac{1}{2}}$ are reciprocals of each other, we can write.

$$\frac{T_{\frac{1}{2}A}}{T_{\frac{1}{2}B}} = \frac{\lambda_B}{\lambda_A} = \frac{N_A}{N_B} \qquad (4.19)$$

**Artificial transmutation of elements.**

By artificial transmutation of elements we mean the production or synthesis of one element from another element by bombarding it with a high-energy sub-atomic particle. The element which is being bombarded is called the **target** (T) and the high-energy particle is called the **projectile** (p). The element produced by transmutation is known as the **product** (P), while another small particle which is generally expelled along with the formation of the product is called the **outgoing particle,** (o). The projectile, on hitting the target nucleus, is captured by it, forming an unstable species known as the **compound nucleus** [C], which then breaks down into the product and the outgoing particle. Thus, the whole process may be represented as :

$$p + T \longrightarrow [C] \longrightarrow P + o + \text{some energy (Q)}.$$

The first example of artificial transmutation was discovered by Rutherford (1919), when he bombarded pure nitrogen gas with high-energy $\alpha$-particles, producing an isotope of oxygen and high-energy protons :

$${}_7N^{14} + {}_2He^4 \longrightarrow [{}_9F^{18}] \longrightarrow {}_8O^{17} + {}_1H^1 + Q.$$

Thereafter, nuclear scientists all over the world undertook the study of artificial transmutation in right earnest, and succeeded in bringing about a very large number of such nuclear reactions. New techniques were developed and used for producing more energetic particles (projectiles) which were very efficient in bringing about artificial transmutations. Projectiles like protons, neutrons, deuterons and $\gamma$-rays are now widely used, along with alpha-particles. Depending on the projectile used and the outgoing particle emitted, artificial transmutation processes are classified now-a-days into a number of types, by writing the projectile and the outgoing particle within a bracket.

Thus, the first artificial transmutation stated before is of $(\alpha, p)$ type. Some typical artificial transmutations are given below :

$(\alpha, p)$ type :

$${}_{5}B^{10}+{}_{2}He^{4} \rightarrow [{}_{7}N^{14}] \rightarrow {}_{6}C^{13}+{}_{1}H^{1}$$
$${}_{13}Al^{27}+{}_{2}He^{4} \rightarrow [{}_{15}P^{31}] \rightarrow {}_{14}Si^{30}+{}_{1}H^{1}$$

$(\alpha, n)$ type :

$${}_{4}Be^{9}+{}_{2}He^{4} \rightarrow [{}_{6}C^{13}] \rightarrow {}_{6}C^{12}+{}_{0}n^{1}$$
$${}_{3}Li^{7}+{}_{2}He^{4} \rightarrow [{}_{5}B^{11}] \rightarrow {}_{5}B^{10}+{}_{0}n^{1}$$
$${}_{11}Na^{23}+{}_{2}He^{4} \rightarrow [{}_{13}Al^{27}] \rightarrow {}_{13}Al^{26}+{}_{0}n^{1}$$

$(n, p)$ type :

$${}_{26}Fe^{56}+{}_{0}n^{1} \rightarrow [{}_{26}Fe^{57}] \rightarrow {}_{25}Mn^{56}+{}_{1}H^{1}$$
$${}_{13}Al^{27}+{}_{0}n^{1} \rightarrow [{}_{13}Al^{28}] \rightarrow {}_{12}Mg^{27}+{}_{1}H^{1}$$
$${}_{30}Zn^{64}+{}_{0}n^{1} \rightarrow [{}_{30}Zn^{65}] \rightarrow {}_{29}Cu^{64}+{}_{1}H^{1}$$

$(n, \alpha)$ type :

$${}_{13}Al^{27}+{}_{0}n^{1} \rightarrow [{}_{13}Al^{28}] \rightarrow {}_{11}Na^{24}+{}_{2}He^{4}$$
$${}_{5}B^{10}+{}_{0}n^{1} \rightarrow [{}_{5}B^{11}] \rightarrow {}_{3}Li^{7}+{}_{2}He^{4}$$
$${}_{3}Li^{6}+{}_{0}n^{1} \rightarrow [{}_{3}Li^{7}] \rightarrow {}_{1}H^{3}+{}_{2}He^{4}$$

$(n, \gamma)$ type :

$${}_{11}Na^{23}+{}_{0}n^{1} \rightarrow {}_{11}Na^{24}+\gamma$$
$${}_{1}H^{1}+{}_{0}n^{1} \rightarrow [{}_{1}H^{2}] \rightarrow {}_{1}H^{2}+\gamma$$

$(p, \alpha)$ type :

$${}_{3}Li^{7}+{}_{1}H^{1} \rightarrow [{}_{4}Be^{8}] \rightarrow 2{}_{2}He^{4}$$
$${}_{4}Be^{9}+{}_{1}H^{1} \rightarrow [{}_{5}B^{10}] \rightarrow {}_{3}Li^{6}+{}_{2}He^{4}$$
$${}_{9}F^{19}+{}_{1}H^{1} \rightarrow [{}_{10}Ne^{20}] \rightarrow {}_{8}O^{16}+{}_{2}He^{4}$$

$(d, n)$ type :

$${}_{13}Al^{27}+{}_{1}D^{2} \rightarrow [{}_{14}Si^{29}] \rightarrow {}_{14}Si^{28}+{}_{0}n^{1}$$
$${}_{6}C^{12}+{}_{1}H^{2} \rightarrow [{}_{7}N^{14}] \rightarrow {}_{7}N^{13}+{}_{0}n^{1}$$
$${}_{3}Li^{7}+{}_{1}H^{2} \rightarrow [{}_{4}Be^{9}] \rightarrow {}_{4}Be^{8}+{}_{0}n^{1}$$

$(d, p)$ type :

$${}_{1}D^{2}+{}_{1}D^{2} \rightarrow {}_{1}H^{3}+{}_{1}H^{1}$$
$${}_{11}Na^{23}+{}_{1}H^{2} \rightarrow [{}_{12}Mg^{25}] \rightarrow {}_{11}Na^{24}+{}_{1}H^{1}$$
$${}_{15}P^{31}+{}_{1}H^{2} \rightarrow [{}_{16}Si^{33}] \rightarrow {}_{15}P^{32}+{}_{1}H^{1}$$

(γ, p) type : $_4Be^9 + \gamma(h\nu) \rightarrow {}_3Li^8 + {}_1H^1$

$_{12}Mg^{25} + \gamma \rightarrow {}_{11}Na^{24} + {}_1H^1$

(γ, n) type : $_1H^2 + \gamma(h\nu) \rightarrow {}_1H^1 + {}_0n^1$

The last two processes are called *photo-disintegration*, since a γ-ray photon acts as the projectile.

**Chemical reaction Vs nuclear reaction.**

Chemical and nuclear reactions differ radically from each other. The more important points of differences are noted below :

1. The magnitude of energy-change in a nuclear reaction is much larger than that involved in a chemical change. For example, the energy of the decay of $_{11}Na^{24}$ is approximately $3.2 \times 10^7$ Kcals/gm-atom, while the heat of formation of one formula-weight of NaCl is only 98.3 Kcals. The difference is of an order of $10^5$.
2. The rate of a nuclear reaction is not at all affected by any factor like pressure, temperature, state of physical occurrence or of chemical combination. But, a chemical reaction is always dependent on one or more of these factors.
3. Every chemical reaction has its own activation energy which must be supplied in order to make it occur. Nuclear reactions do not necessarily require activation energy and occurs spontaneously.
4. The nuclear properties of the different isotopes of an element is different, while their chemical properties are identical. Thus, the chemical property of radio-phosphorus, $_{15}P^{30}$, and ordinary stable phosphorus, $_{15}P^{31}$, are the same. But, $_{15}P^{30}$ is a positron-emitter, while $_{15}P^{31}$ is non-radioactive.
5. A chemical reaction occurs as a result of some change in the outer sphere of the atom. It involves any of the processes of electron-transfer, sharing or overlap of electron-orbitals in the valence-shell. Hence, elements keep their identity in chemical reactions. But, the nuclear reactions originate in the inner sphere, *i.e.* in the nuclei of the atoms, and as a result, the identity of the elements change due to nuclear reactions (the reactions involving emission of neutron and γ-rays being exempted).

**Artificial radioactivity or induced radioactivity.**

While studying the effect of bombardment of $\alpha$-particles on light atom targets like boron, aluminium *etc.*, I. Curie and F. Joliot (1934) noticed that the products exhibited a positron-activity, along with the neutron-emission expected in ($\alpha$, n) type of reactions. They found that, though the neutron-emission ceased when the bombardment is stopped, the positron-activity continued and decreased rather slowly with time. On careful analysis of the reactants and the products, they explained the observations as follows :

$$\begin{tikzcd}[column sep=small]
{}_5B^{10}+{}_2He^4 \arrow[r] & {}_7\overset{*}{N}^{13} \arrow[d, "T_{\frac{1}{2}}=9{\cdot}9\text{ minutes}"] & +{}_0n^1\ \text{(conventional } \alpha\text{, n reaction)} \\
& {}_6C^{13}+{}_{+1}e^0 &
\end{tikzcd}$$

$$\begin{tikzcd}[column sep=small]
{}_{13}Al^{27}+{}_2He^4 \arrow[r] & {}_{15}\overset{*}{P}^{30} \arrow[d, "T_{\frac{1}{2}}=2{\cdot}55\text{ minutes}"] & +{}_1n^1\ (\alpha\text{, n reaction)} \\
& {}_{14}Si^{30}+{}_{+1}e^0 &
\end{tikzcd}$$

The nuclei marked with asterix are radioactive and these are the first examples of radioactivity artificially induced in elements whose naturally occuring isotopes are stable and non-radioactive.

The positron-activity of ${}_7\overset{*}{N}^{13}$ and ${}_{15}\overset{*}{P}^{30}$ are easily explained by comparing the n : p ratio of each of them with that of their stable, naturally occurring isotopes ${}_7N^{14}$ and ${}_{15}P^{31}$ respectively. As is discussed before, the lower n : p ratio is increased by the emission of a positron which reduces the number of protons and increases the number of neutrons at one stroke.

The discovery of induced radioactivity opened a new horizon to the nuclear scientists. Nearly 1500 artificial radio elements have been produced by now and put to numerous important uses. The artificial radio nucleides behave exactly as their non-radioactive counterparts. Their decay follows the first order rate law and they have their characteristic half-lives and disintegration constants by which they can be identified.

Artificial radio elements can also be produced by the bombardment with other projectiles like neutron and deuteron. A few examples are :

$$\begin{array}{l} {}_{13}\mathrm{Al}^{27} + {}_{0}n^{1} \rightarrow {}_{11}{}^{*}\mathrm{Na}^{24} + {}_{2}\mathrm{He}^{4} \text{ (n, } \alpha \text{ reaction)} \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad\quad {}_{12}\mathrm{Mg}^{24} + {}_{-1}e^{0} \end{array}$$

$$\begin{array}{l} {}_{6}\mathrm{C}^{12} + {}_{1}\mathrm{D}^{2} \longrightarrow \left\langle \begin{array}{l} \longrightarrow [{}_{7}\mathrm{N}^{14}] \rightarrow {}_{6}\mathrm{C}^{13} + {}_{1}\mathrm{H}^{1} \text{ (d, p reaction)} \\ \longrightarrow [{}_{7}\mathrm{N}^{14}] \rightarrow {}^{*}{}_{7}\mathrm{N}^{13} + {}_{0}n^{1} \text{ (d, n reaction)} \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\quad\;\; {}_{6}\mathrm{C}^{13} + {}_{+1}e^{0} \end{array} \right. \end{array}$$

**Specific activity.**

The specific activity of a radioactive material is expressed as the number of disintegrations per second or as the number of curies per gram of the substance being examined. The specific activity of pure elemental radium is 1 curie per gram, *i.e.* 1 gram of pure radium undergoes $3.7 \times 10^{10}$ disintegrations per second.

**Isotopic labelling of compounds.**

Labelling a particular element in a molecule is done by changing its natural isotopic composition by artificial means. Ordinary carbon contains 1.1 per cent of the $C^{13}$ isotope and $10^{-10}\%$ of $C^{14}$. If the proportion of any one of these isotopes, say $C^{14}$, is increased, the carbon is said to be **labelled** with respect to the isotope which has been enriched. The acetic acid molecule, $CH_3COOH$, contains two different carbon atoms, and any one or both of them can be labelled with $C^{14}$ or $C^{13}$. If we want to follow the course of a reaction, such as decarboxylation, in which $CO_2$ is eliminated, we may label the carboxyl carbon atom with $C^{14}$. This can be done by reacting methyl chloride with sodium cyanide or silver cyanide labelled with $C^{14}$ :

$$\begin{array}{l} \mathrm{CH_3Cl} + \mathrm{NaC^{14}N} \rightarrow \mathrm{CH_3C^{14}N} + \mathrm{NaCl} \\ \qquad\qquad\qquad\qquad\quad \downarrow \text{ Hydrolysis} \\ \qquad\qquad\qquad\quad\;\; \mathrm{CH_3C^{14}OOH}. \end{array}$$

If this labelled $CH_3C^{14}OOH$ is made to undergo decarboxylation, the evolved $C^{14}O_2$ will exhibit radioactivity ($C^{14}$ is a positron-emitter), which can be followed easily, using a suitable counting equipment. Similarly, amino acids may be labelled with $N^{15}$ and phosphorus compounds can be labelled with $P^{30}$ and so on. Labelling does not necessarily involve radio-isotopes, – non-radioactive isotopes can also be used for such purposes. In labelling oxygen atoms in a compound, the $O^{18}$ isotope is frequently used.

**Nuclear Fission.**

In 1938, Otto Hahn and S. Strassmann observed that uranium, on bombardment with slow neutrons, broke up into two nuclei of atomic numbers 56 and 36, liberated 2-3 neutrons and also released a tremendous amount of energy. The element of atomic number 56 is barium (${}_{56}Ba^{147}$) and that with atomic number 36 is krypton (${}_{36}Kr^{86}$). The nuclear transmutation is represented as :

$${}_{92}U^{235} + {}_{0}n^{1} \longrightarrow [{}_{92}U^{236}] \longrightarrow {}_{56}Ba^{147} + {}_{36}Kr^{86} + 3\,{}_{0}n^{1} + Q.$$

Such a process of breaking up of the nucleus of a heavy atom into two nuclei of comparable mass, accompanied by the release of a large amount of energy and a few small particles like neutron, is called a **nuclear fission.**

It was found that the mass of barium atom + krypton atom + three neutrons is **less** than that of the parent ${}_{92}U^{235}$ + the bombarding neutron. This difference is found to be nearly 0.215 amu per atom of uranium-235. According to Einstein's theory, this mass is converted into energy, which is of the order of 200 Mev.

We have seen above that 2-3 neutrons are liberated per fission. If the 3 neutrons hit three more $U^{235}$ nuclei, we can get 9 neutrons, which in their turn can produce fission of nine $U^{235}$ nuclei, and so on. Thus, a chain reaction would begin, which will multiply very fast and a huge amount of energy will be released in a very short time. Such a chain reaction is schematically represented in Fig. 4.9.

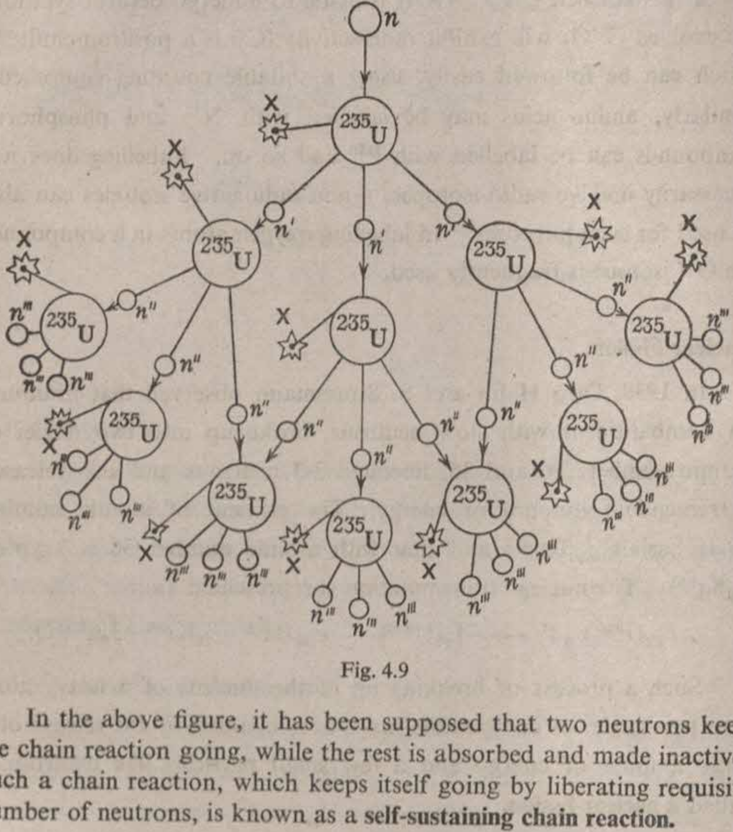


Fig. 4.9

In the above figure, it has been supposed that two neutrons keep the chain reaction going, while the rest is absorbed and made inactive. Such a chain reaction, which keeps itself going by liberating requisite number of neutrons, is known as a **self-sustaining chain reaction.**

For such a chain reaction to proceed, the $_{92}U^{235}$ lump should have a certain minimum mass, below which, most of the neutrons produced will escape out of the lump and the chain reaction will slow down and finally stop. This minimum mass of the $U^{235}$ lump, which will just maintain the self-sustaining chain reaction, is called the **critical mass of $U^{235}$.**

**Transuranic elements (The man-made elements).**

The heaviest element occurring in nature is uranium, which has two major isotopes $U^{238}$ and $U^{235}$. We know that $U^{235}$ undergoes fission by slow-neutron bombardment. But, $U^{238}$ absorbs neutron, forming the $U^{239}$ isotope : $U^{238}(n,\gamma)\rightarrow U^{239}$.

This $U^{239}$ isotope is a neutron-rich nucleide and hence emits a β-particle, forming $_{93}Np^{239}$, which in its turn, emits a β-particle, forming $_{94}Pu^{239}$ :

$$_{92}U^{239} \xrightarrow{-\beta^-} {}_{93}Np^{239} \xrightarrow{-\beta^-} {}_{94}Pu^{239}.$$

But, the nuclear scientists did not stop at plutonium, and made attempts to synthesise elements of even higher atomic numbers, which were realised in practice with the fabrication of enormously powerful particle-accelerators like the **linear accelerator**, the **cyclotron**, the **synchrotron**, the **bevatron** etc. Uptil now, all elements having atomic numbers 94 – 105 have been synthesised. These are variously known as the transuranic elements, the actinides or the man-made elements. The following table contains the names, symbols, atomic numbers and the mass numbers of the transuranic elements :

(TRANSURANIC ELEMENTS)

| Name | Symbol | Atomic No. | Atomic mass |
|---|---|---|---|
| Neptunium | Np | 93 | 231—241 |
| Plutonium | Pu | 94 | 232—243 |
| Americium | Am | 95 | 237—244 |
| Curium | Cm | 96 | 238—245 |
| Berkelium | Bk | 97 | 243—245 |
| Californium | Cf | 98 | 244—246 |
| Einsteinium | Es | 99 | 246—256 |
| Fermium | Fm | 100 | 250—256 |
| Mendelevium | Mv | 101 | ~256 |
| Nobelium | No | 102 | ~251 |
| Lawrencium | Lw | 103 | ~257 |
| Kurchatovium | Ku | 104 | ~260 |
| Hahnium | Hn | 105 | Not known with certainty. |

**Spallation.**

In the case of fission, the slow neutron is captured by $U^{235}$ nucleus, which subsequently breaks down into two nuclei of comparable masses, accompanied by 2-3 neutrons. But, when atoms of medium mass-numbers are bombarded by high-energy projectiles, the target nucleus is broken down to several fragment (20 – 30 smaller nuclei and nucleons). This phenomenon is known as *spallation*. This name has its origin in the verb "to spall", meaning *to break up by clipping off small fragments.* It was discovered by G.T. Seaborg and his co-workers in 1947. An example of the spallation process is

$$_{29}Cu^{63} + {}_2He^4(400 \text{ Mev}) \longrightarrow {}_{17}Cl^{37} + 14\,{}_1H^1 + 16\,{}_0n^1.$$

The major product-nucleus produced by the spallation process generally possesses a mass 10—20 units lower than the mass of the target nucleus.

The difference between *fission* and spallation is twofold—(i) the spallation reaction is not self-sustaining like the fission process and (ii) the change in mass of the most massive product-nucleus in a spallation reaction is not so great as that observed in a fission process.

The difference from an ordinary nuclear reaction lies in the magnitude of the change in mass of the major product-nucleus. In an ordinary nuclear reaction, the change in mass of the target nucleus is rarely above 1 – 4 mass units, while that observed in spallation lies in the range of 10 – 20 mass units.

**Nuclear fusion or thermonuclear reactions.**

The nuclear fusion process is one, in which the combination or fusion of two nuclei results in the formation of a larger nucleus, accompanying energy-change of large magnitude. From the study of the binding energy curve of the elements (Fig. 4.9), it is clear that, if two nuclei of low mass are fused together, energy will be liberated, *i.e.*, fusion is an energy-liberating process in the low mass-number range, but not so in the high mass-number region. Also, two large nuclei, due to their high nuclear charges, will repel each other very strongly as the two approach each other, and it becomes practically impossible to bring about fusion of two large nuclei. Thus, for all practical purposes, fusion of two light nuclei like ${}_1H^1$, ${}_1H^2$, ${}_1H^3$, with the formation of the very stable nucleus ${}_2He^4$, will be good examples of the nuclear fusion process.

But, to bring about the fusion of even such light nuclei, the individual nuclei must be sufficiently energised so as to overcome the very strong mutual repulsion of the positively charged nuclei. This is done by raising the temperature of the fuel material to $10^6 - 10^7$ °K. To attain such high temperature within a very short time, the fuel material is surrounded by a sheath of $U^{235}$ which is allowed to undergo fission chain-reaction, and the heat generated thereby forces the hydrogen isotopes to undergo fusion and liberate huge amount of energy. The major fusion reactions that occur may be represented as :

$$
\begin{aligned}
{}_1H^2+{}_1H^2 &\rightarrow {}_2He^4+24.9\text{ Mev},\\
{}_1H^3+{}_1H^2 &\rightarrow {}_2He^4+{}_0n^1+17.8\text{ Mev},\\
{}_1H^3+{}_1H^1 &\rightarrow {}_2He^4+20\text{ Mev},\\
{}_1H^3+{}_1H^3 &\rightarrow {}_2He^4+2{}_0n^1+11\text{ Mev}.
\end{aligned}
$$

The function of fission chain-reaction is to produce the required high temperature and thereby cause fusion, and it is known as **primer** or **trigger**. Since the initiation of the process of fusion is attained by raising the temperature of the materials, it is also known as **thermonuclear reaction.** The energy liberated in fusion is much greater than that in fission; but, since it is much more difficult to control the energy of fusion processes, they have yet to be utilised for practical purposes. The source of energy in stars, including the sun, is believed to be due to the conversion of hydrogen into helium by fusion processes.

## USES OF RADIO-ISOTOPES.

Uses of isotopes, both radioactive and non-radioactive, pervade different fields of science, and have even entered into the every-day life of a common man. Perhaps the greatest achievements of the nuclear scientists to-day is the successful production and the uses of the large number of isotopes in different spheres of human life. The uses of isotopes may be broadly classified into the following major groups : (1) biological, medicinal and agricultural uses, (2) uses in chemical analysis, (3) dating studies like determination of ages of rocks and minerals and of old relics, and (4) studies in the mechanisms of dynamic processes, like mechanism of chemical reactions and of attainment of equilibria.

Radio-isotopes are generally favoured over stable isotopes because they are easily detected even in small concentrations and the course of their movement can be constantly monitored.

### (1) Uses in biological, medicinal and agricultural fields.

Understanding of protein metabolism has been achieved by the use of radio-isotopes. The formation of a complex protein molecule by the condensation of different aminoacids has been followed by using one or more aminoacids labelled with ${}_7N^{15}$ (a $\beta$-emitter). The process of assimilation of a protein has also been followed in the same way by isolating the degraded products, some of which contained atoms labelled previously.

Radioactive $Co^{60}$ (a $\gamma$-emitter), radium and radioactive gold are widely used for the treatment of cancer. The radiations emitted from these nuclei destroy the malignant cells in the body in preference to the normal cells and hence heal up the affected parts.

Transportation of a particular nutrient, say phosphorus, from the root to leaves and its overall distribution to different parts of the plant body have been followed by feeding the plant with phosphatic fertilizers containing a small amount of ${}_{15}P^{30}$ isotope.

**(2) Uses in chemical analysis.**

In chemical analysis, radio-isotopes are generally used to find out the extent of completion of an analytical procedure. For example, when lead is precipitated from aqueous solution by the addition of a soluble chromate, a very small amount of lead remains in solution and causes error, however small it may be. If radioactive lead of known amount and specific activity is added to the solution previously, the measurement of activity of the precipitated lead chromate will tell us how much of lead is left in solution.

A trace constituent in a solid alloy can be accurately determined by converting that constituent (along with the other elements present) into its radioactive isotope by neutron bombardment and measuring the rate of decay of the radio-isotope of that element produced thereby.

The specific names of some of the analytical techniques utilising radio-isotopes are : (i) Isotope dilution method, (ii) radiometric analysis and (iii) activation analysis.

**(3) Dating of minerals, rocks and old relics.**

The ratio of ${}_6C^{12}$ and ${}_6C^{14}$ (produced by neutron bombardment of ${}_7N^{14}$ due to cosmic ray interaction) is $10^{12} : 1$ in nature. Carbon, in the form of $CO_2$, containing the above ratio of ${}_6C^{12}$: ${}_6C^{14}$, is taken up by plants during photosynthesis. Thus, in living plants, the $C^{12} : C^{14}$ ratio is $10^{12} : 1$. Animals which feed on the plants and those which consume the animals also have the same $C^{12} : C^{14}$ ratio in their life time. When the plant or animal dies, it cannot take up carbon any more, and henceforth the ${}_6C^{14}$ goes on decaying without being replenished and so its amount gradually decreases depending on its life period. Thus, the determination of the $C^{12} : C^{14}$ ratio can tell us when the plant or the animal had died.

Let us consider an example. In an old Egyptian mummy, the $C^{12} : C^{14}$ ratio was found to be half of that in living human being. Calculate the approximate time when the man had died. Given, $T\frac{1}{2}$ of $C^{14}=5760$ years.

We know that, $\lambda = \frac{0.693}{T\frac{1}{2}} = \frac{0.693}{5760}$ year. Let t be the required time period.

According to the conditions of the problem, $\frac{N_0}{N} = \frac{1}{0.5}$.

We know that, $2.303 \log\frac{N_0}{N} = \lambda t$ ; or, $\log\frac{N_0}{N} = \frac{\lambda t}{2.303}$ ; or, $\frac{2.303}{\lambda} \times \log\frac{N_0}{N} = t$.

$$\therefore\ t=\frac{2.303\times0.3010\times5760}{0.693}=5750 \text{ years.}$$

So, the man had died 5750 years ago.

(4) **Uses in mechanistic studies.**

The mechanism of photosynthesis by plants from carbon dioxide and water, with the help of chlorophyll, has been elucidated by the use of ${}_{8}O^{18}$ isotope. The reaction leading to the synthesis of carbohydrates and release of oxygen is :

$$6CO_2+6H_2O \rightarrow C_6H_{12}O_6+6O_2.$$

The question is, where from this oxygen comes—from carbon dioxide or from water? This has been clarified by adding a small amount of water, labelled with $O^{18}$ isotope. On analysis of the products, it was found that all $O^{18}$ isotope used as water is evolved as gaseous oxygen. If, however, the $CO_2$ is labelled with $O^{18}$, the evolved oxygen does not contain any $O^{18}$. Hence, it was proved that it is the oxygen in water which comes off as gaseous oxygen.

CHAPTER V

# ACID-BASE AND SOME RELATED PHENOMENA

The term **acid** originated from the Latin word **acetum** which means vinegar. Thus, substances resembling vinegar in *sour taste* and in their capability of changing blue litmus to red were called acids. The word **alkali** (which was later replaced by the more general term **base**) came from the Arabic term for **ashes of plants,** as those substances were first isolated from plant ashes. Alkalis or bases were substances which neutralised acids and could change red litmus to blue. Thus, from the very beginning of the recognition of acid-base phenomenon, acids and bases were defined in terms of satisfaction of certain experimental facts.

With the progress of time, newer aspects of the acid-base phenomenon were revealed, and workers in the field put forward several concepts in order to rationalise the diverse observations. In this chapter, we shall discuss four such concepts, treated in the order of increasing importance.

**Arrhenius concept :** All of us are familiar with Arrhenius' theory of electrolytic dissociation. Arrhenius recognised acids and bases as electrolytes and defined an acid as a hydrogen-containing compound which ionises in water to yield hydrogen ions. A base is defined as one which releases hydroxyl ions in aqueous solution. Since acids and bases destroy the distinctive properties of each other by the process of neutralisation, *neutralisation*, in this concept, is nothing but the reaction of hydrogen and hydroxyl ions, producing practically undissociated water. Since water is the most important and most widely used solvent, Arrhenius concept could explain many aspects of the acid-base phenomenon in aqueous medium and helped us to look into the quantitative aspects of the acid-base phenomenon with special reference to *acid-base strength*, *neutralisation* and *hydrolysis*. However, it suffered from the following defects which necessitated new and more comprehensive concepts of acid-base reactions :

(1) Only those compounds were regarded as bases which contain hydroxyl ions, *i.e.* basic character was confined to the hydroxides

only, and even the oxides of strongly electropositive metals were not regarded as bases.

(2) The entire acid-base phenomenon was confined to aqueous medium only and the process of neutralisation, leading to the formation of salt and water, could not take place in any other medium except water. But, it is well-known that neutralisation can take place in many non-aqueous solvents and even in absence of solvents *e.g.*

$$NH_3(g)+HCl(g) = NH_4Cl(s).$$

(3) The bare proton, due to its high charge density (charge/volume or charge/radius), can not exist as such in water which is dipolar and have lone pairs of electrons on the oxygen atom, which will co-ordinate with the $H^+$ion, forming the hydronium ion, $H_3O^+$.

**Solvent-system concept** : This concept originated from Frankland's attempts to extend the acid-base phenomenon to non-aqueous medium. It has been noted long back that, all ammonium salts behave as acids in **liquid ammonia solution,** while the amides exhibited basic character in it. From the study of the electrical properties of liquid ammonia, it was recognised that ammonia undergoes auto-ionization as :

$$\underset{\text{solvent}}{2NH_3} \rightleftharpoons \underset{\text{solvent cation}}{NH_4^+} + \underset{\text{solvent anion}}{NH_2^-}$$

According to this concept, an **acid** is a substance which, on dissolution in a solvent, **yields the solvent cation,** and materials **yielding the solvent anion** are **bases** in that medium. Thus, all ammonium salts are acids in liquid ammonia because they dissociate as :

$$NH_4X \rightleftharpoons \underset{\text{solvent cation}}{NH_4^+} + X^-$$

and the amides behave as bases in liquid ammonia due to their ionisation,

$$MNH_2 \rightleftharpoons M^+ + \underset{\text{solvent anion}}{NH_2^-}$$

The neutralisation process is thus a combination of the solvent cation and the solvent anion, leading to the formation of undissociated solvent molecules :

$$NH_4^+ + NH_2^- \rightleftharpoons 2NH_3.$$

Table 5.1. contains the auto-ionization processes of some important non-aqueous solvents, and enlists a number of compounds, some of which behave as acids and some as bases in these media.

TABLE 5·1

| Solvent (liquid) | Auto-ionization process | A few compounds behaving as acids (the cation is written within bracket). | A few compounds behaving as bases (the anion is given within bracket). |
|---|---|---|---|
| $H_2O$ | $H_2O+H_2O \rightleftharpoons H_3O^++OH^-$ | All protonic acids like HCl, $HNO_3$, $H_2SO_4$, $H_3PO_4$ *etc.* ($H^+$). | All hydroxides, basic oxides like NaOH, $Ca(OH)_2$, $Na_2O$, CaO *etc.* ($OH^-$). |
| $NH_3$ | $NH_3+NH_3 \rightleftharpoons NH_4^++NH_2^-$ | All Ammonium salts. ($NH_4^+$) | All amides. ($NH_2^-$). |
| $SO_2$ | $SO_2+SO_2 \rightleftharpoons SO^{+2}+SO_3^{2-}$ | Thionyl compounds like $SOX_2$ (X=Cl, Br *etc.*) ($SO^{+2}$). | All sulphites like $Na_2SO_3$, $CaSO_3$ *etc.* ($SO_3^{2-}$) |
| $N_2O_4$ | $N_2O_4+N_2O_4 \rightleftharpoons 2NO^++2NO_3^-$ | Nitrosyl compounds like NOX (X=Cl, Br *etc.*) ($NO^+$). | All nitrates like $KNO_3$, $NaNO_3$ *etc.* ($NO_3^-$). |

The solvent-system concept covers all the aspects of Arrhenius concept, and in addition, it extends and explains acid-base behaviour in non-aqueous solvents. Thus, it is an advancement over Arrhenius concept. But, inspite of this advantage, it is far from being adequate to explain the acid-base phenomenon as a whole. It makes acid-base behaviour fully dependent on solvents and their ionization characteristics, and does not recognise *intrinsic* acidic or basic character of any substance.

**The protonic concept or Brönsted-Lowry concept :**

This concept, proposed simultaneously by Brönsted and Lowry, was the first to recognise the intrinsic acidic or basic properties of substances and consider the acid-base phenomenon without the essential involvement of a solvent. According to this concept, an acid is a substance which can donate or release one or more protons, and a base is a substance which can accept or combine with one or more protons; *i.e.*, *proton-donors* are acids and *proton-acceptors* are bases.

Thus, HCl is an acid because it is capable of donating a proton to a suitable acceptor and even in absence of the acceptor (base), it is still considered as an acid due to its *intrinsic proton-donating character*. The $NH_3$ molecule and the $OH^-$-ion are bases, as both of them can *accept a proton*.

Since acids tend to donate proton, the negative ion left after the splitting off of the proton, should be considered as a base, *i.e.*,

$$\begin{array}{lcl} \underset{\text{Acid}}{\mathrm{HA}} & \rightleftharpoons & \mathrm{H^+} + \underset{\text{Base}}{\mathrm{A^-}} \\ \underset{\text{Acid}}{\mathrm{HCOOH}} & \rightleftharpoons & \mathrm{H^+} + \underset{\text{Base}}{\mathrm{HCOO^-}} \end{array}$$

Any acid HA tends to release a proton and form the anion A- which, in turn can form the acid by accepting a proton. This can be represented as :

$$\begin{array}{c} \mathrm{HA} \\ \text{Acid} \end{array} \underset{+H^+}{\overset{-H+}{\rightleftarrows}} \begin{array}{c} \mathrm{A} \\ \text{Base} \end{array}$$

Since $A^-$ is capable of accepting a proton in order to form the acid, $A^-$ is a base. Such an acid-base pair, interconvertible by the loss or gain of a proton, is called a **conjugate acid-base** pair. Thus, the base $A^-$ is the conjugate base of the acid HA, while HA is the conjugate acid of the base $A^-$. Similarly, $Cl^-$ and $NO_3^-$ are the conjugate bases of the acids HCl and $HNO_3$ respectively.

In an analogous manner, a base is represented as a proton-acceptor.

$$\begin{array}{c} \mathrm{B} \\ \text{base} \end{array} \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} \begin{array}{c} \mathrm{BH^+} \\ \text{acid} \end{array}$$

$$\begin{array}{c} \mathrm{NH_3} \\ \text{base} \end{array} \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} \begin{array}{c} \mathrm{NH_4^+} \\ \text{acid} \end{array}$$

$$\begin{array}{c} \mathrm{NaOH} \\ \text{base} \end{array} \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} \begin{array}{c} (\mathrm{Na^+ + H_2O}) \\ \text{acid} \end{array}$$

Thus, $BH^+$ is the conjugate acid of the base B, and B is the conjugate base of the acid $BH^+$. Similarly, $NH_4^+$ is the conjugate acid of the base $NH_3$ and $Na^+$ is the conjugate acid of the base NaOH.

The process of neutralisation, therefore, involves the transfer of a proton from the acid to the base which accepts it :

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{NH_3} \longrightarrow \underset{\text{acid}_2}{NH_4^+} + \underset{\text{base}_1}{Cl^-}$$

$$\underset{\text{acid}_1}{HNO_3} + \underset{\text{base}_2}{OH^-} \longrightarrow \underset{\text{acid}_2}{H_2O} + \underset{\text{base}_1}{NO_3^-}$$

The acids and bases are not limited to neutral molecules; ions can also behave as acids or bases, *e.g.*

$$\underset{\text{acid}_1}{HCO_3^-} + \underset{\text{base}_2}{OH^-} \rightleftharpoons \underset{\text{acid}_2}{H_2O} + \underset{\text{base}_1}{CO_3^{2-}}$$

$$\underset{\text{acid}_1}{NH_4^+} + \underset{\text{base}_2}{CH_3COO^-} \rightleftharpoons \underset{\text{acid}_2}{CH_3COOH} + \underset{\text{base}_1}{NH_3}$$

Thus, all acid-base reactions involve two acids and two bases, *i.e.*, two conjugate acid-base pairs, and take place as a result of competition of bases to accept protons from the acids, leading to a kind of equilibrium indicated in the last two examples.

From the foregoing discussion, it is quite clear that **stronger is the acid, the weaker is its conjugate base**, because if the conjugate base is strong, then it will be reluctant to part with the proton and hence decrease the proton-donating character of the acid, making it a weak one. Thus, $Cl^-$ is a weak base because HCl is a strong acid, while the acetate ion, $CH_3COO^-$, is a strong base as acetic acid is a weak acid. Similarly, the conjugate acid of a strong base is weak and that of a weak base is strong. Hence, $Na^+$ is a weak acid because NaOH is a strong base and $NH_4^+$ is a fairly strong acid as $NH_3$ is a weak base.

It should be noted here that, *all proton-transfer reactions proceed predominantly in the direction in which the weaker acid and the weaker base are formed.* So, we can write :

$$\text{Stronger acid} + \text{stronger base} \rightleftharpoons \text{Weaker acid} + \text{weaker base}$$

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

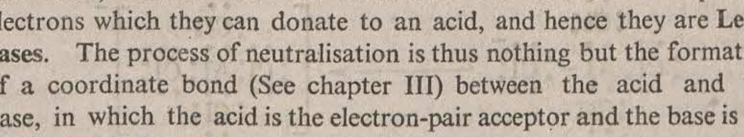
$NH_4^+$ is a weaker acid than HCl while $Cl^-$ is a weaker base than $NH_3$.

The Brônsted concept or the protonic concept recognises the intrinsic acid or base character of substances and tells us that acid-base reactions are not necessarily dependent on the solvent. But, its excessive emphasis on the presence of the proton in all acids excludes substances like $SO_2$, $AlCl_3$, $N_2O_4$, $SOCl_2$, NOCl, $COCl_2$ *etc.* from the category of acids, although these are definitely involved in acid-base phenomenon.

This theory can satisfactorily explain the processes like neutralisation, hydrolysis, relative strengths of acids and bases. These aspects of this theory will be discussed later in this chapter.

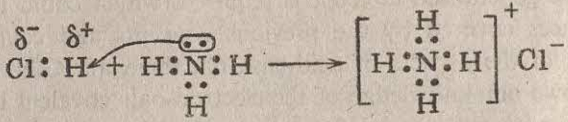
**Lewis Concept :** We have already discussed three different acid-base concepts and have pointed out the limitations of each of them. We have found that all the concepts do not agree fully as to what substances should be called acids or bases. Some consider the involvement of a suitable solvent essential for the manifestation of acid-base phenomenon, while the others do not. So, it is quite natural that, a more generalised concept is required, which could include all the substances covered by the previous concepts and could explain all or most of the aspects of acid-base phenomena. G.N. Lewis, to whom we owe our knowledge of the electron-pair covalent bond, was the first to note the special features in the electronic structures of acids and bases, which were the real causes of their acidic and basic properties. According to the **Lewis concept, an acid is an electron-pair acceptor** and **a base is an electron-pair donor.** Thus, structurally, an acid is such an entity which can accommodate a pair of electrons on it, *i.e., it must have at least one vacant orbital in its valence-shell where it can accommodate an electron-pair*. The proton, which is recognised as an acid by all the concepts, has its 1*s*-orbital vacant. It can attain the helium duplet structure by accepting or accommodating one pair of electrons and hence the proton ($H^+$) is an acid in the Lewis sense also. Similarly, the hydroxyl ion ($OH^-$ ) and the amide ion ($NH_2^-$) are bases, because both of them have one or more lone pair of electrons which they can donate to an acid, and hence they are **Lewis bases.** The process of neutralisation is thus nothing but the formation of a coordinate bond (See chapter III) between the acid and the base, in which the acid is the electron-pair acceptor and the base is the electron-pair donor.

Such a neutralisation process is the reaction between boron trifluoride and ammonia :



Here, in $BF_3$ molecule, the central atom boron has six electrons and hence is two short of the octet, and has the tendency to accept a pair of electrons to complete the octet. Hence, it is a Lewis acid. Ammonia, possessing a lone pair of electrons, has an inherent tendency to donate it to an acceptor, and hence, it is a Lewis base. When $BF_3$ and $NH_3$ come close to each other, the lone pair of the $NH_3$ molecule is donated to the vacant 2*p*-orbital of the electron-deficient boron atom of the molecule $BF_3$. As a result of this, a coordinate bond is formed between boron and nitrogen, leading to the destruction of the acidic properties of $BF_3$ and the basic character of $NH_3$, which is the process of neutralisation.

Another common example of such neutralisation reaction is the reaction between $NH_3$ and HCl :



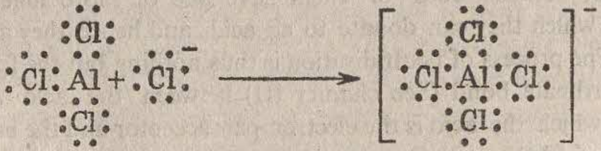
Of the various classes of substances which act as Lewis acids, the most important ones are :

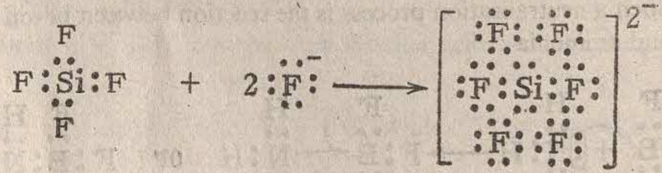
1. Simple cations, *e.g.* $Na^+$, $Mg^{+2}$, $Al^{+3}$, $Fe^{+2}$, $Fe^{+3}$ *etc.*

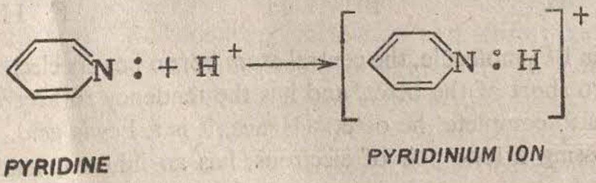
2. Electron-deficient compounds which have an incomplete octet round the central atom, *e.g.* $BF_3$, $BCl_3$, $AlCl_3$ *etc.*

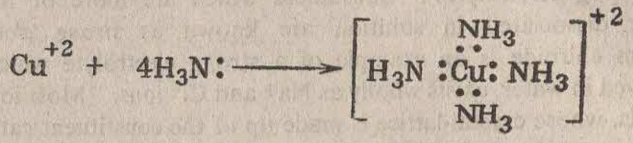
3. Compounds in which the octet on the central atom can be expanded, *e.g.*, $PF_3$, $SiF_4$, $SnCl_4$ *etc.* $PF_3$ can form $PF_5$ and $PF_6^-$ with fluoride ions, $SiF_4$ can form $SiF_6^{2-}$ with fluoride ions.

A few such examples of neutralisation in the Lewis sense are presented below :









$$\mathrm{Cu}^{+2} + 4\mathrm{H_3N}\!: \longrightarrow \left[\begin{array}{c} \mathrm{NH_3} \\ \mathrm{H_3N}\,:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cu}}}:\,\mathrm{NH_3} \\ \mathrm{NH_3} \end{array}\right]^{+2}$$

All the Lewis bases, capable of donating one or more electron-pairs to Lewis acids, are also termed as **ligands.**

Thus, the Lewis concept encompasses in one sweep all the known phases of acid-base phenomenon included in the Arrhenius concept, the general theory of the solvent-system and the Bronsted-Lowry concept, and releases them from their dependence on proton and on solvents in which the reactions take place. In addition, it includes the complex-formation reactions between the metal ions and the ligands, and even those cases of oxidation-reduction which involve the loss or gain of electrons in pairs. **Lewis acids** and **Lewis bases** find extensive use in organic chemistry. A Lewis acid is termed an *electrophile* or *electroplilic reagent* and the Lewis base is called a *nucleophile* or a *nucleophilic reagent* in the domain of organic reactions. Aluminium chloride, boron trifluoride, ferric chloride and such other Lewis acids are used in acid-catalysed organic reactions in place of Bronsted acids like HF and $H_2SO_4$, and in many cases they are much more effective than the latter ones.

But, it should be noted here that, inspite of its more fundamental and comprehensive character, the Lewis concept suffers from a defect of quite a serious nature. It cannot be applied to explain and illustrate the quantitative aspects of the acid-base phenomenon like the relative strengths of acids and bases. In discussing the quantitative aspects of the acid-base phenomena, we have to make use of the Bronsted theory or the protonic concept, as most of the common acids are protonic acids and most of the bases are proton-acceptors.*

## Quantitative aspects of the acid-base and some other related phenomena.

Before entering into actual details of the quantitative aspects of the acid-base phenomena, we should be familiar with the terms like **strong** and **weak electrolytes, degree of dissociation** *etc.*, and must have some knowledge about **OSTWALD'S DILUTION LAW.**

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* Discussions on Hard and Soft Acids and Bases (SHAB concept) is placed at the end of this chapter.

**Strong electrolytes :** Substances which are more or less completely dissociated in solution are known as *strong electrolytes.* Sodium chlroide is an example of a strong electrolyte which, when dissolved in water, exists wholly as $Na^+$ and $Cl^-$ ions. Most ionic compounds, whose crystal-lattice is made up of the constituent cations and anions, are strong electrolytes. Most of the mineral acids like HCl, $HNO_3$, $H_2SO_4$ *etc.* and many of the bases like NaOH, KOH, $Ca(OH)_2$ *etc.* fall in the category of strong electrolytes, because they are completely dissociated into the constituent ions.

**Weak electrolytes** : Substances which are only partially dissociated into their constituent ions in solution are called *weak electrolytes.* Acetic acid is an example of such a weak electroyte. When dissolved in water, acetic acid is partially and reversibly dissociated as :

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+.$$

This means that, not all the molecules of acetic acid, but only a fraction of them, are dissociated in solution. The fraction of the total number of molecules of a weak electrolyte that is dissociated in solution, is known as the *degree of dissociation* of that electrolyte (here acetic acid).

**Ostwald's dilution law and relative strengths of acids and bases.**

Since the dissociation of any weak electrolyte is an equilibrium reaction, the law of mass action can be applied to calculate the equilibrium constant, known as the **dissociation constant of the electrolyte.** Let us consider the case of dissociation of acetic acid.

$$\begin{array}{lccc} & CH_3COOH & \rightleftharpoons \; CH_3COO^- & + \; H^+ \\ \text{At the start :} & 1 & 0 & 0 \\ \text{At equilibrium :} & (1-\alpha) & \alpha & \alpha \end{array}$$

Let one gram-mole of acetic acid be dissolved in V litres of water and let '$\alpha$' be the fraction of acetic acid dissociated at equilibrium. Then, as a result of the dissociation, '$\alpha$' moles of the acetate ion, $CH_3COO^-$, '$\alpha$' moles of hydrogen ion, $H^+$ and $(1-\alpha)$ moles of undissociated acetic acid are present in the system at equilibrium. So, the concentration of undissociated acetic acid, $[CO_3COOH]=\frac{(1-\alpha)}{V}$, that of acetate ion, $[CH_3COO^-]=\frac{\alpha}{V}$ and that of hydrogen ion, $[H^+]=\frac{\alpha}{V}$.

Applying the law of the mass action to this system, we can write

$$Ka = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad \cdot\cdot \quad \cdot\cdot \quad (5.1)$$

$$\text{or, } K_a = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{(1-\alpha)}{V}} = \frac{\alpha^2}{(1-\alpha)V} \quad \ldots \quad \ldots \quad (5.2)$$

Since concentration, $C=\frac{1}{V}$, the eqn. 5.2, can be written as

$$K_a = \frac{\alpha^2 C}{(1-\alpha)} \quad \ldots \quad \ldots \quad \ldots \quad (5.3)$$

Here, $K_a$ is the dissociation constant or ionisation constant of acetic acid. From equation 5.2, it is evident that, higher the value of $K_a$, greater is the strength of the acid (or any other electrolyte being studied). The equation 5.2, which tells us how the degree of dissociation varies with dilution, is the **Ostwald's dilution law.** It has been found by experiments that this law is well-obeyed by the weak electrolytes. Since $K_a$ is an equilibrium constant, it is constant only at a constant temperature.

For a weak electrolyte, for which the degree of dissociation is very small, $(1-\alpha)$ may be taken as almost equal to 1, *i.e.* $(1-\alpha)=1$. Under such conditions, eqn. 5.3 becomes,

$$\alpha^2 C = K_a \; ; \; \text{or, } \alpha = \sqrt{\frac{K_a}{C}} \quad \ldots \quad \ldots \quad (5.4)$$

Eqn. 5.4 can also be written as, $\alpha=\sqrt{K_a.V}$ .. .. (5.5)

Thus, for the solution of a weak electrolyte at any particular temperature, the degree of dissociation is inversely proportional to the square-root of concentration and directly proportional to the square-root of the dissociation constant.

**Strength of acids.**

The strength of a protonic acid is generally measured by its tendency to release a proton in the equilibrium reaction, $HA \rightleftharpoons H^+ + A^-$. The equilibrium constant, of this reaction, $K = \frac{C_{H^+} C_{A^-}}{C_{HA}}$, is a quantitative measure of the above tendency, and it is known as the ionisation constant of the acid[1]. Direct measurement of K can be done only in the presence of a base (B) in the system to accept the $H^+$ donated by the acid (HA). Thus, it is necessary to consider an equilibrium of the type, $HA + B \rightleftharpoons BH^+ + A^-$, where B is the reference base. In such measurements (generally in the cases of weaker acids), water is generally taken both as the solvent and the base, so that the value of the equilibrium constant becomes, $K = \frac{C_{H_3O^+} C_{A^-}}{C_{HA} C_{H_2O}}$. Since $C_{H_2O}$ can be taken to be constant, the value of K becomes equal to $\frac{C_{H_3O^+} C_{A^-}}{C_{HA}}$ in sufficiently dilute solutions and in solvents like water having high values of dielectric constant. Such a method gives good results for the values of K, although they are somewhat approximate. But, such values may be satisfactorily used to judge the relative strengths of weaker protonic acids.[2]

For stronger acids like HCl or $H_2SO_4$, the above method of determining the ionisation constant cannot be applied in water solution. In such cases the values of K come out to be indeterminately large. This is due to the fact that water is quite basic with respect to these acids which leads the reaction $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ practically fully to the right. This property of the solvent, which is known as the *levelling effect*, becomes more and more pronounced as the basicity of the solvent increases, so that benzoic acid, a typical weak acid, behaves as a very strong one in liquid ammonia solvent. Measurements in aprotic solvents (like benzene) also present certain problems like the formation of ion-pairs and higher-order associated species. These were due to the low dielectric constants of the solvents. So, acidic solvents have been used to measure the relative strengths of the acids.* By conductivity measurements in acetic acid solvent, the strengths of the mineral acids have been found to be in the order,

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3.$$

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[1] In the equation, the C-terms, which refer to the concentrations of the respective species, should actually be substituted by their activities. But in very dilute solutions, the activities may be replaced by the concentrations.

[2] An accurate method for the determination of the thermodynamic ionisation constant of protonic acids is based on the e.m.f. measurements, using a cell of the type,

$$Pt, H_2 \mid HA(m_1),\ NaA(m_2),\ NaCl(m_3) \mid AgCl, Ag.$$

* In fact, this method also fails sometimes due to fact that some solutes react with the solvents to give more complicated products than would be obtained from a simple proton transfer.

Recently, a quantitative scale of acid and base strengths for any given solvent system has been suggested. A comparison between two acids or bases is made by comparing the fraction ($\alpha$) of the electrolyte ionised, summed over molar concentrations from 0 to 1. This is accomplished by taking the integral (S) of the Ostwald dilution law in this range. This fraction equals unity for a strong acid or base (completely ionised in solution) and approaches zero for a very weak acid or base. For example, a comparison between hydrochloric acid and acetic acid may be made as follows : In water, $S_{HCl}=1$ and $S_{ACOH}=8{\cdot}4\times10^{-3}$. So, $S_{HCl}/S_{ACOH}=119$, and hydrochloric acid is estimated to be 119 times stronger than acetic acid. For weak acids, $S_1/S_2$ is nearly equal to $\sqrt{K_1/K_2}$.

**Relative strengths of acids in the light of the protonic concept**

It has already been pointed out that, inspite of its fundamental character and versatility, *Lewis concept* cannot be utilised to explain the relative strengths of acids and bases. For the explanation of relative strengths of acids and bases, it is better to take the help of *Bronsted's protonic concept*, especially so, because most of the acids generally encountered are protonic acids and most of the bases are proton acceptors.

**Strength of acids and their molecular structures**

For the sake of a fruitful discussion on their relative strengths, acids are conveniently classified into the following general types :

(1) *Hydracids.*
(2) *Oxyacids.*
(3) *Organic acids.*

(1) **Hydracids*** : Hydracids can be represented by the general formula $H_nX$ (where n is a small integer) in which X is a non-metal atom occurring in the right hand side of the periodic table. It is well-known that the strength of the protonic acid HX depends on its ease and extent of ionisation as

$$HX \rightleftharpoons H^+ + X^-.$$

Hence, the factors which control the extent or ease of this ionisation process, regulate the strength of such protonic acids. Two such factors are,

(i) electronegativity of the element X
and (ii) atomic radius (or atomic volume) of the element X.

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* It must be remebered that here we are considering the pure acids and not their aqueous solutions.

(i) *Influence of the magnitude of electronegativity of the element X on the strength of the acid HX :*

Higher value of the electronegativity of the element X causes greater displacement of the H—X bond-pair towards the atom X ($\overset{+\delta}{H}—\overset{-\delta}{X}$). As a result of such displacement of the bond-pair, the dipole moment value of the hydracid HX is increased significantly. This increased dipole moment facilitates the dissociation of the acid HX as $HX \rightleftharpoons H^+ + X^-$ and hence increases its strength as an acid. In other words, it may be said that, *the strength of the acid HX depends on the electronegativity of X.*

Magnitude of the dipole moment of HX depends primarily on two factors : (a) on magnitude of the charge on H or X generated due to the greater electronegativity of X and (b) on the H—X bond distance (d) which depends on the atomic radius of X. The effect of the electronegativity of X on the acid strength has already been discussed. The effect of the H—X bond distance on the strength of the acid HX will be discussed now.

(*ii*) *Effect of the atomic radius (atomic volume) of X on the strength of the acid HX :*

It is well-known that the atomic radii of the elements of any periodic group increase with the increase in atomic number as we move downwards, and electronegativity of the members decrease in the same direction. The following table contains the atomic radii (Å) and the electronegativity values (Pauling scale) of the elements of Gr. VIB of the periodic table.

TABLE 5.2

| Elements of Gr. VIB | O<br>At. No.=8 | S<br>At. No.=16 | Se<br>At. No.=32 | Te<br>At. No.=52 |
|---|---|---|---|---|
| Atomic radius (Å) | 0·73 | 1·02 | 1·16 | 1·35 |
| Electronegativity (Pauling scale) | 3·5 | 2·5 | 2·4 | 2·1 |

The observed trend in the acid strength of hydracids of Gr. VIB elements is $H_2Te > H_2Se > H_2S > H_2O$,

i.e. the strength of the hydracids of Gr.VIB elements increases down the group, though electronegativity of the Gr. VIB elements decreases in that direction (see above table). It can be seen from the atomic radii data that atomic radii of the Gr. VIB elements increase down the group. Thus, in this case we face a situation in which the electronegativity factor and the atomic radius factor, both of which regulate the strength of the acid HX, act in opposite directions, the observed trend corresponding with the atomic radius factor. The reason behind this observation is that, the effect of increase of H—X bond-distance overshadows the effect of the increase in electronegativity acting in the opposite direction. For the same reason, the strength of the hydracids of Gr. VIIB elements exhibit the trend

$$HI > HBr > HCl.$$

(2) **Oxyacids** : Oxyacids may be represented by the general formula $HO_nX$ (n=1, 2, 3 etc.), where X is an electronegative element. The oxyacids of chlorine furnish a very good example of an oxyacid series.

n=1 ; $HO_nX$ = HOCl, hypochlorous acid
n=2 ; $HO_nX$ = $HClO_2$, chlorous acid
n=3 ; $HO_nX$ = $HClO_3$, chloric acid
n=4 ; $HO_nX$ = $HClO_4$, perchloric acid

The strength of the oxyacid represented by any particular general formula (say, HOX, where n=1) depend primarily on the *effective electronegativity** of the element X and its atomic volume or radius.

For the elements of a periodic group, the strengths of the X—O—H -type acids depend mostly on the electronegativity of the element X. This is the reason why the observed trend in acid strength of the H—O—X-type acids of the Gr. VIIB elements are

$$HOCl > HOBr > HOI.$$

Higher electronegativity of Cl, compared to that of Br, results in the greater displacement of the O—Cl bond pair towards the Cl-atom, as compared to the displacement of the bond pair of the O—Br bond towards Br. As a result of such electron displacement, the O-atom attracts the bond-pair of the H—O bond towards itself with greater force, leading to the facile dissociation of the O—H hydrogen as $H^+$. For similar reasons, HOBr is stronger than HOI.

Increase in the number of oxygen atoms in the oxyacids of any particular element results in the increase in their acid strength. Thus, the strengths of oxyacids of chlorine exhibit the trend

$$HClO_4 > HClO_3 > HClO_2 > HClO.$$

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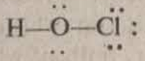
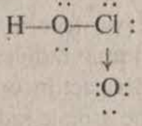
*It is the actual electronegativity value in the particular compound being considered and is chiefly dependent on the oxidation state of the element X.

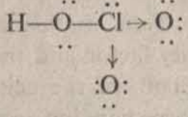
All these acids are monobasic acids and can be represented by the following bond structures :



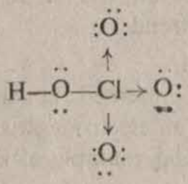
(HOCl)



(HC O$_2$)



(HClO$_3$)



(HClO$_4$)

In $HClO_4$, the three bond pairs of the three Cl→O bonds remain displaced towards the more electronegative oxygen atoms and thereby increases the effective electronegativity of the central atom Cl considerably. As a result of this increase in effective electronegativity, the Cl-atom in $HClO_4$ strongly attracts the bond pair of the H—O bond towards itself and thereby helps the O—H-hydrogen readily dissociate as $H^+$ ($HClO_4 \rightleftharpoons H^+ + ClO_4^-$). The gradual decrease in the number of atoms of oxygen attached to the central element chlorine in $HClO_3$, $HClO_2$ and HClO, leads to the decrease of the effective electronegativity of the chlorine atom in them. As a result of this effect, the dissociation of the O—H-hydrogen becomes less facile and the strength of these acids decreases in the direction

$$HClO < HClO_2 < HClO_3.$$

Another way of explaining the observed trend in the acid strength of the oxyacids is to adduce such variation to the magnitude of the oxidation state of the central element X,— higher oxidation state of the central element causing greater acid strength. Thus, the observed trend in acid strength,

$$\overset{+7}{HClO_4} > \overset{+5}{HClO_3} > \overset{+3}{HClO_2} > \overset{+1}{HClO}$$

is due to the fact that in the above acids the oxidation state of chlorine being +7, +5, +3 and +1 respectively.

The observed trends in the strength of the oxyacids of phosphorus, arsenic, sulphur and selenium

$$H_3PO_4 > H_3PO_3$$
$$H_3AsO_4 > H_3AsO_3$$
$$H_2SO_4 > H_2SO_3$$
$$H_2SeO_4 > H_2SeO_3$$

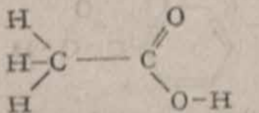
can be explained similarly.

(3) **Organic acids** : Strength of organic acids are mostly regulated by the operation of *inductive effect* and *resonance*. For the convenience of our present discussion, organic acids may be classified into (a) aliphatic carboxylic acids, (b) aromatic carboxylic acids and (c) phenols. In (a), the inductive effect plays the leading role in determining the acid strength. In (b) and (c), resonance is the factor which generally predominates when both inductive effect and resonance are operative in the same molecule.

(a) *Aliphatic carboxylic acids* : Aliphatic monocarboxylic acids are represented by the general formula RCOOH which undergo dissociation as,

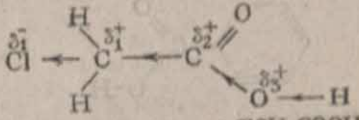
$$RCOOH \rightleftharpoons H^+ + RCOO^-.$$

Acetic acid is considered as the representative member of this series. The structure of acetic acid (a) and that of monochloro acetic acid (obtained by the replacement of one H-atom of the methyl group of acetic acid by the strongly electronegative element chlorine) is given below :



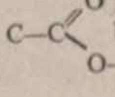
Acetic acid (CH$_3$COOH)
$K_a = 1{\cdot}8 \times 10^{-5}$ (25°C)

(a)

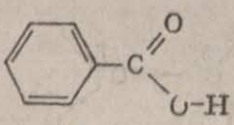


Monochloro acetic acid ClCH$_2$COOH
$K_a = 1{\cdot}38 \times 10^{-3}$ (25°C)

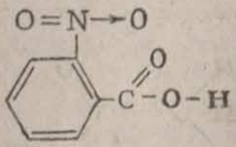
(b)

Chlorine, being much more electronegative than carbon, the bond-pair of the C—Cl bond in monochloro acetic acid is attracted towards the chlorine atom due to the operation of inductive effect. As a result, a small negative change $\delta^-_1$ accumulates at the chlorine end of the C—Cl bond, an equivalent positive charge $\delta^+_1$ being localised on the carbon atom. This carbon atom, containing $\delta^+$ positive charge, attracts the bond pair of the C—C bond of  $\mathrm{C{-}C}\begin{smallmatrix}\nearrow\!\!\!\!/ \,O\\ \searrow O{-}H\end{smallmatrix}$ bond towards itself and thereby generates a positive charge $\delta_2^+$ ($\delta_2^+ < \delta_1^+$) on the carbonyl-carbon atom. This carbonyl-carbon atom, containing $\delta_2^+$ positive charge, will, in its turn, attract the C—O bond pair towards itself, resulting in the generation of a small positive charge $\delta_3^+$ ($\delta_3^+ < \delta_2^+$) on the C—O-oxygen atom. This oxygen atom with residual positive charge will cause facile dissociation of the O—H proton of the —COOH group by attracting the O—H bond pair towards itself. The whole sequence of these situations is illustrated in figure (b). Thus, $ClCH_2COOH$ is a much stronger acid than $CH_3COOH$ due to the operation of inductive effect in it. For the same reason, $Cl_2CHCOOH$ is a stronger acid than either $CH_3COOH$ and $ClCH_2COOH$. So, it can be mentioned generally that, if one or more H-atoms of an aliphatic acid are replaced by the corresponding number of electronegative atoms (e.g. F, Cl, Br etc.) or groups ($-NO_2$, $-SO_3H$), the substituted acid will be stronger than the parent acid. Among such substituted aliphatic acids, the relative strength will depend on the electronegativity of the substituent atom or group. This is why the observed trend of acid strength among the monohalogeno acetic acids is $FCH_2COOH >$ $ClCH_2COOH > BrCH_2COOH$.

(b) **Aromatic carboxylic acids :** Benzoic acid can be considered as the representative of aromatic carboxylic acids. Structures of benzoic acid and *o*-nitrobenzoic acid are given below.

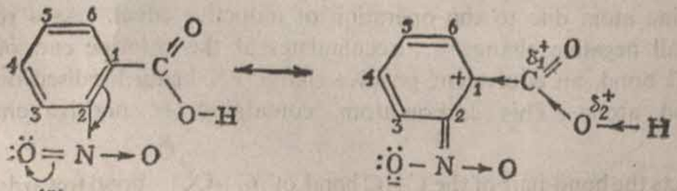


Benzoic acid



Orthonitro benzoic acid

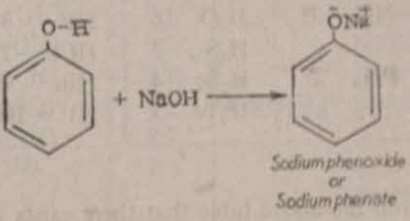
As an acid, *o*-nitrobenzoic acid is much stronger ($K_a = 6{\cdot}7 \times 10^{-3}$) than benzoic acid ($K_a = 6{\cdot}3 \times 10^{-5}$). The reasons for the greater strength of *o*-nitrobenzoic acid may be explained in the following way with the help of the figure presented below.



(I) (II)

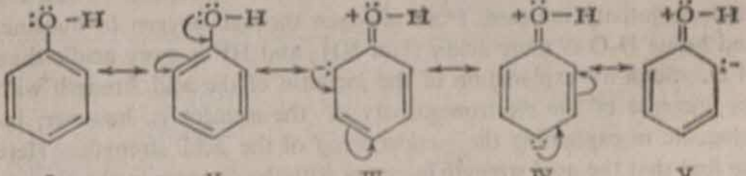
A scrutiny of the above figure reveals that the positive charge generated on the nitrogen atom of the $-NO_2$ group due to electromeric effect results in the shift of the $\pi$-electrons of the benzene ring (between 1 and 2-carbon atoms) towards the C−N bond connecting the nitro group with the C(2) carbon atom of the benzene ring. This process results in the formation of the C=N double bond. As a result of such an electron-shift, positive charge is generated on the C(1) carbon atom of the benzene ring with which the carbonyl group is attached. Then, due to the operation of extended inductive effect as shown in the figure, the release of the −O−H-hydrogen of the −COOH group as a proton is facilitated. Resonace among the two structures (resonating forms) stabilise the molecule as a whole and the sequence of electronic changes are also facilitated by resonance and leads to the greater acidity of *o*-nitrobenzoic acid. For similar reasons, groups like $-NO_2$, −COOH, $SO_3H$, NO, Cl, Br, etc. (with +I effect), when present in ortho or para positions with respect to the −COOH group in an aromatic acid, increase the strength of the resultant acid.

(c) **Phenols :** Phenols are very weakly acidic. They do not react with $NaHCO_3$ or $KHCO_3$. They react as acids only with strong bases like NaOH and KOH, forming phenoxide compounds :



Phenol

Feeble acidic character of phenol may be explained as follows :



A careful scrutiny of the above figure reveals that the phenol molecule can be represented as the resonance hybrid of the resonating forms I-V. Of these five structures, the oxygen atom of the phenolic —OH group assumes +ve charge due to resonance. This positively charged oxygen quite naturally attracts the bond pair of the O—H bond towards itself and makes the removal of the hydrogen atom as $H^+$ possible. However, contribution of the structures III-V, containing the charged O-atom, being small, the OH proton is only feebly acidic.

In the case of aliphatic hydroxy compounds or alcohols (R—O—H), removal of $H^+$ from the —OH group is not possible and hence they are not acidic. They are neutral. For $CH_3$—O—H, the representative member of the aliphatic alcohols, resonating structures containg positively charged oxygen atom can not be constructed and hence, removal of $H^+$ from the aliphatic alcohols is not possible.

**General trend in acid strength.**

(A) **Strength of hydracids** : The pK values of the hydrides of some of the elements of Groups V, VI and VII of the periodic table are given below :

TABLE 5.3

| Gr. V | Gr. VI | Gr. VII |
|---|---|---|
| $NH_3$ 35 | $H_2O$ 16 | HF 3 |
| | $H_2S$ 7 | HCl −7 |
| $PH_3$ 27 | $H_2Se$ 4 | HBr −9 |
| | $H_2Te$ 3 | HI −10 |

It is seen from the above table that there exists definite trend in the strengths of hydracids as we go *across a period* or *down a group* in the periodic table. Considerable increase in the acid strength occurs in going from left to right across a period. This is obviously due to the increase in electronegativities of the non-metals concerned. Thus, the electronegativity increases from nitrogen through oxygen to fluorine, and hence $H_2O$ is more acidic than $NH_3$ and HF is more acidic than $H_2O$. Such an explanation of the increase of the acid strength with the increase of the electronegativity of the element is, however, inadequate in explaining the *vertical trend* of the acid strength. Here we find that the acid strength increases with the decrease in the electronegativity of the element. Thus, pure HI in a stronger acid than pure HF, although fluorine is much more electronegative than iodine. It seems reasonable, therefore, to conclude that electronegativity is certainly not the only factor that influences the acid strength of the hydracids. It is quite logical that the strength of a hydracid is associated with the ease with which it can give up its hydrogen atom as a proton. This is obviously augmented by the increase of the dipole moment of the molecule which arises from an increased electronegativity of the non-metal. But, this is also facilitated by the weakening of the bond between hydrogen and the non-metal in the molecule of the hydracid. The bond strength of hydrogen halides at 0°A in the gaseous state decreases gradually from 141 Kcal/mole for HF to 70·6 Kcal/mole for HI. This decrease in bond strength parallels the increase in the acid strengths of the halogen hydracids.

### (B) Strength of oxyacids.

According to the pK values of the inorganic oxyacids, they are found to form four distinct groups, as shown below :

TABLE 5.4

| Group I | | | Group II | | |
|---|---|---|---|---|---|
| Class & formula | Example | pK | Class & formula | Example | pK |
| $X(OH)_m$ | $Ge(OH)_4$ | 8·6 | $XO(OH)_m$ | $PO(OH)_3$ | 2·1 |
| | $As(OH)_3$ | 9·2 | | $HPO(OH)_2$ | 1·8 |
| | $Te(OH)_6$ | (8·8) | | $AsO(OH)_3$ | 2·3 |
| | $Cl(OH)$ | 7·2 | | $SO(OH)_2$ | 1·9 |
| | $Br(OH)$ | 8·7 | | $SeO(OH)_2$ | 2·6 |
| | $I(OH)$ | 11·0 | | $ClO(OH)$ | 2·0 |
| | | | | $IO(OH)_5$ | 1·6 |

| Group III | | | Group IV | | |
|---|---|---|---|---|---|
| Class & formula | Example | pK | Class & formula | Example | pK |
| $XO_2(OH)_m$ | $SO_2(OH)_2$ | (−3) | $XO_3(OH)_m$ | $ClO_3(OH)$ | (−10) |
| | $SeO_2(OH)_2$ | (−3) | | | |
| | $IO_2(OH)_2$ | 0·8 | | | |
| | $ClO_2(OH)_2$ | −1·0 | | | |
| | $NO_2(OH)$ | −1·4 | | | |

It is clearly evident from the above table that there exists a correlation between the structure of the acids and the groups to which they belong. It is seen that, in the members of the first group, all the oxygen atoms in the molecule of the acid are bonded to the hydrogen atoms, *i.e.* all of them are parts of the hydroxyl groups. The members of the second or the subsequent groups, contain one or more non-hydroxyl oxygen atoms, and as the number of non-hydroxyl oxygen atoms in the molecule of the acid increases, there is a regular increase in the acid strength. It is also noted from the table that the number of hydroxyl groups in the molecule of the acid has little effect on the acid strength. So, it may be concluded that the number of non-hydroxyl oxygen atoms in the molecule of an oxyacid determines its strength.* It is also seen from the table that for any particular general formula of the oxyacids, the acid strength decreases with the increase of the size of the central atom. Thus, with Cl(OH), Br(OH) and I(OH), the pK values are 7·2, 8·7 and 11·0 respectively.

It has also been suggested that acid strength of the oxyacids depends not only on the number of non-hydroxyl oxygen atoms in their molecules, but also on the formal charge on the central atoms. The following empirical relationship has been proposed for the pK values of these acids :

$$\mathrm{pK} = 8{\cdot}0 - m \times 9{\cdot}0 + n \times 4{\cdot}0,$$

where $m$ is the formal charge on the central atom and $n$ is the number of non-hydroxyl oxygen atoms in the molecule. On this basis, the oxyacids can be classified as shown below :

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* This has been generalised by an empirical rule which states, "The value of the first ionisation constant of an oxyacid (and hence its acid strength) is determined by the value of $m$ in the formula $XO_m(OH)_n$. If $m$ is zero (*i.e.* there is no excess of oxygen atoms over hydrogen atoms, as in $B(OH)_3$), the acid is very weak ($K_1 \leqq 10^{-7}$); for $m = 1$, the acid is weak ($K_1 \cong 10^{-2}$) ; for $m=2$ ($K_1 \cong 10^{3}$) or $m=3$($K_1 \cong 10^{8}$), the acid is strong.

The underlying principle of this rule can be understood from the following examples of the oxyacids of chlorine. In HOCl, the force of attraction between $H^+$ and $ClO^-$ is that of O—H valance bond. But, in $HClO_2$ the force between $H^+$ and either of the two oxygen atoms of $ClO_2^-$ ion will necessarily be smaller than that of an O—H valence bond, because the total attraction for the $H^+$ is divided between the two oxygen atoms. Hence, $HClO_2$ is expected to be more highly dissociated than HOCl. $HClO_3$ will, for the same reason, be more highly dissociated than $HClO_2$, since the total attraction for the $H^+$ would be divided among three oxygen atoms.

TABLE 5.5

| Class | Example | $pK_1$ |
|---|---|---|
| $m=0; n=1$ | $H_4GeO_4$ | 8·6 |
| | $H_3AsO_3$ | 9·2 |
| | $H_4TeO_6$ | 8·8 |
| | HClO | 7·2 |
| | HBrO | 8·7 |
| | HIO | (11·0) |
| $m=1; n=1$ | $H_3PO_4$ | 2·1 |
| | $H_3PO_3$ | 1·8 |
| | $H_3AsO_4$ | 2·3 |
| | $H_2SO_3$ | 1·9 |
| | $H_2SeO_3$ | 2·6 |
| | $HClO_2$ | 2·0 |
| | $H_5IO_6$ | 1·6 |
| $m=2; n=2$ | $H_2SO_4$ | — |
| | $H_2SeO_4$ | — |
| | $HIO_3$ | 0·8 |
| | $H_2P_4O_7$ | 0·9 |

**Common-ion effect.**

When a strong electrolyte is added to the solution of a weak electrolyte having an ion in common, the degree of dissociation of the weak electrolyte is considerably changed. Thus, if sodium acetate is added to an aqueous solution of acetic acid, the salt is almost completely dissociated into $Na^+$ and $CH_3COO^-$, as a result of which, the position of the equilibrium existing in the solution of acetic acid

$$CH_3COOH \rightleftharpoons CH_3COO^- + H \quad .. \quad .. \quad (5.6)$$

is changed and a new equilibrium is established, in which the relation,

$Ka = \dfrac{[CH_3COO^-] [H^+]}{[CH_3COOH]}$ still holds good.

In order to maintain the constancy of Ka, the $H^+$ ions combine with $CH_3COO^-$ ions, forming undissociated acetic acid, and thereby decreases the degree of dissociation of the acid. Thus, the addition of a stronger electrolyte to a weak electrolyte in solution, having an ion in common, depresses the degree of dissociation of the weak electrolyte, and this phenomenon is known as the **common-ion effect.** So, the degree of dissociation of the weak acetic acid is further decreased by the addition of sodium acetate to it, the acetate ion being the *common ion* in this case.

**Some applications of the common-ion effect in inorganic analysis.**

The common-ion effect is frequently utilised in inorganic analysis, and we will now discuss a few of its applications in qualitative analysis.

**I. Selective precipitation of Gr. IIA and Gr. IIB (of analytical chemistry) metal sulphides in presence of the metal ions of the subsequent groups.**

In the routine qualitative analysis of the basic radicals, the Gr. IIA ($Hg^{+2}$, $Cu^{+2}$, $Bi^{+3}$, $Pb^{+2}$, $Cd^{+2}$) and the Gr. IIB ($As^{+3}$, $Sb^{+3}$, $Sn^{+2}$) ions are precipitated as their sulphides in acid medium. The reagent $H_2S$, which supplies the $S^{2-}$ ions, is a weak electrolyte and dissociates in aqueous solution as :

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{2-}$$

The over-all dissociation process, yielding $S^{2-}$ ions, is thus,

$$H_2S \rightleftharpoons 2H^+ + S^{2-}.$$

If a strong acid like HCl is added to a solution containing dissolved $H_2S$, the HCl will dissociate completely, releasing a large amount of $H^+$ ions (depending on the amount of HCl added). Under such conditions, due to the effect of the common ion ($H^+$), the dissociation of $H_2S$ will be suppressed and the concentration of $S^{2-}$ ion will be lowered considerably. In practice, the acidity is kept near 0.3N, at which the dissociation of $H_2S$ is suppressed and is so regulated that, the $[S^{2-}]$ is just sufficient to precipitate all the Gr. IIA and IIB metal ions as sulphides, but the sulphides of the metals of the subsequent groups are not precipitated, as they require larger $[S^{2-}]$.

In fact, with such low concentrations of the sulphide ion, the values of the solubility products of the sulphides of Groups IIA and IIB are exceeded (as these values are very small) and they are, therefore, precipitated. The values of the solubility products of the sulphides of the metals of the subsequent groups, being much larger, are not reached by such small concentrations of the sulphide ion and hence they are not precipitated.

**II. Precipitation of Gr. IIIA metal ions ($Fe^{+3}$, $Al^{+3}$, $Cr^{3+}$) as their hydroxides.**

The reagent used in the precipitation of $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ is the weak base $NH_4OH$. But, if $NH_4OH$ alone is added in excess, then the [$OH^-$] ions produced in solution due to its dissociation, $NH_4OH \rightleftharpoons NH_4^+ + OH^-$, are sufficient to precipitate the hydroxides of the Gr. IIIB metal ions also. In order to prevent the precipitation of the Gr. IIIB hydroxides, and to precipitate the Gr. IIIA hydroxides selectively, sufficient $NH_4Cl$ is added to the solution before adding $NH_4OH$. $NH_4Cl$, being a salt, dissociates practically completely, furnishing considerable amount of the common ion, $NH_4^+$. As a result, the dissociation of $NH_4OH$ is decreased due to the operation of the common-ion effect, and the resultant [OH] comes to a level which is just sufficient to precipitate $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$, but is not enough to precipitate the hydroxides of the Gr. IIIB metal ions ($Mn^{+2}$, $Co^{+2}$, $Ni^{+2}$, $Zn^{+2}$). Here also, the lower values of the solubility products of $Al(OH)_3$, $Fe(OH)_3$ and $Cr(OH)_3$ are exceeded by the amount of $OH^-$ ions produced under the specified conditions and they are precipitated. The values of the solubility products of the hydroxides of Group IIIB metals, being considerably higher, are not reached by such low concentrations of the hydroxide ions and hence they are not precipitated.

**III. Precipitation of Gr. IV metal ions ($Ca^{+2}$, $Sr^{+2}$ and $Ba^{+2}$) as their carbonates in presence of magnesium ($Mg^{+2}$) ions.**

The reagent used in the precipitation of $CaCO_3$, $SrCO_3$ and $BaCO_3$ is $(NH_4)_2CO_3$ in ammoniacal medium. When $Mg^{+2}$ is also present in solution, addition of $(NH_4)_2CO_3$ alone will result in the precipitation of $MgCO_3$ along with the Gr. IV metal carbonates. To prevent this, the dissociation of ammonium carbonate, $(NH_4)_2CO_3 \rightleftharpoons 2NH_4^+ + CO_3^{2-}$, is depressed by adding a large amount of the common ion, $NH_4^+$, through the addition of $NH_4Cl$ prior to the addition of the $(NH_4)_2CO_3$ reagent. The operation of common-ion effect regulates the [$CO_3^{2-}$] to a value which is just sufficient to precipitate the Gr. IV metal carbonates, without precipitating $MgCO_3$ which requires larger [$CO_3^{2-}$]. The value of the solubility product of $MgCO_3$ is much higher than those of the carbonates of Group IV metals. The values of the solubility products of $CaCO_3$, $SrCO_3$ and $BaCO_3$ are exceeded by the amount of $CO_3^{-2}$ ions present in the medium under the stipulated conditions, but that of $MgCO_3$ is not reached. Hence, $CaCO_3$, $SrCO_3$ and $BaCO_3$ are precipitated in Group IV, but not $MgCO_3$.

**Ionization of Water.**

Even the most rigorously purified water conducts electric current, though very feebly, and suffers electrolysis. This definitely proves that the water molecules undergo some feeble dissociation. That these ions are $H^+$ and $OH^-$ is indicated by the facts that many reactions which are catalysed by acids and bases are also catalysed by water. Thus, dissociation of water may be represented as :

$$H_2O \rightleftharpoons H^+ + OH^-,$$

or, better by $2H_2O \rightleftharpoons H_3O^+ + OH^-$. .. .. (5.7)

(Henceforth, whenever we will write $[H^+]$, we will really mean $H_3O^+$ by it.) The expression for the dissociation constant, K, of this process can be obtained by applying the law of mass action :

$$K = \frac{[H^+][OH^-]}{[H_2O]} \quad .. \quad .. \quad (5.8)$$

$$\text{or, } K[H_2O] = [H^+][OH^-] \quad .. \quad .. \quad (5.9)$$

As water is a very weak electrolyte and undergoes dissociation to a very small extent (*i.e.*, the degree of dissociation of water, $\alpha$, is very small), concentration of undissociated water molecules $[H_2O]$ is practically constant. Thus, we may consider $K[H_2O] = K_W$, as another constant. So, the eqn. 5.9 now becomes $K_W = [H^+][OH^-]$ .. (5.10). This constant $K_W$ is called the *ionic product of water*. **It must be kept in mind that this $K_W$ is a constant at constant temperature for any particular aqueous solution,** acidic or alkaline. Since the dissociation of one molecule of water yields one $H^+$ and one $OH^-$, in pure water

$$[H^+]=[OH^-] \text{ ; or, } K_W=[H^+]^2=[OH^-]^2.$$

The value of $K_W$ at 25°C is $1 \times 10^{-14}$ (approx.). So, in pure water,

$$[H^+]=[OH^-] = \sqrt{K_W} = \sqrt{10^{-14}}=10^{-7} \text{ gm-ions/litre.}$$

Since $K_W = [H^+][OH^-]$,

$$[H^+]=\frac{K_W}{[OH^-]} \quad .. \quad .. \quad (5.11)$$

$$\text{and } [OH^-]=\frac{K_W}{[H^+]} \quad .. \quad .. \quad (5.12)$$

Thus, for an aqueous solution at any temperature, if either $[OH^-]$ or $[H^+]$ is known, the other can be easily calculated, using the value of $K_W$ at that temperature.

### Relation between $K_W$ and K of water.

One must not confuse the ionic product of water, $K_W$, with its dissociation constant, K.

We have already found that,

$$K_W = [H^+] \times [OH^-]$$

$$\text{and} \quad K = \frac{[H^+] \times [OH^-]}{[H_2O]}$$

$$\text{So,} \quad K = \frac{K_W}{[H_2O]} \qquad \qquad (5.13)$$

In one litre of water, *i.e.* in 1000 grams (approx.) of water, the number of moles of $H_2O$ present is $\frac{1000}{18} = 55{\cdot}55$.

Thus, in pure water $[H_2O] = 55{\cdot}55$. So, $K = \frac{K_W}{55{\cdot}55}$ ;

$$\text{or,} \quad K_W = 55{\cdot}55 \text{ K}.$$

$$\therefore \; K = \frac{1 \times 10^{-14}}{55{\cdot}55} = 1{\cdot}8 \times 10^{-16} \text{ (approx.) at } 25^\circ\text{C}.$$

### Quantitative evaluation of acidity or alkalinity of a solution : the pH concept.

Depending on the amount of acid present, the concentration of $H^+$ of a solution can vary over a wide range. The hydrogen-ion concentration of $\frac{N}{1000}$ HCl solution is $1 \times 10^{-3}$ gm-ions/litre, that of $\frac{N}{6000}$ solution of HCl is $1{\cdot}66 \times 10^{-4}$ gm-ions/litre and that of an $\frac{N}{60000}$ solution is $1{\cdot}66 \times 10^{-5}$. This method of expressing hydrogen-ion concentration of solutions is not very convenient, as it yields values which are rather cumbrous. It is difficult to get an idea of the state of acidity or alkalinity of the solution from the values expressed in this manner, So, the concept of pH was first introduced by Sorensen in order to overcome the difficulties mentioned above. **pH of an aqueous solution is defined to be equal to the negative logarithm** (to the base 10) **of the hydrogen-ion concentration of the solution,** *i.e.*

$$pH = -\log_{10}[H^+] \qquad \qquad (5.14)$$

$$\text{or} \quad [H^+] = 10^{-pH} \qquad \qquad (5.15)$$

Thus, the pH of a solution of $[H^+]=1\times10^{-3}$ is,

$$pH=-\log[H^+]=-\log(1{\cdot}0\times10^{-3})=3.$$

Similarly, pH of the solution with $[H^+]=1{\cdot}66\times10^{-4}$ gm-ions/litre is given by,

$$pH=-\log(1{\cdot}66\times10^{-4})=3{\cdot}78$$

and the pH of a solution with $[H^+]=1{\cdot}66\times10^{-5}$ gm ions/litre is, $pH=-\log(1{\cdot}66\times10^{-5})=4{\cdot}78$.

Hence, we note that pH is a simple and more convenient way of expressing the $[H^+]$ of a solution, and from the last two cases we realise that a *tenfold change* in the hydrogen-ion concentration of a solution results in a *change of one unit of its pH*. A solution of pH=1, has $[H^+]=10^{-1}$ and a solution of pH=2, has $[H^+]=10^{-2}$ and so on. Thus, **as pH increases by one unit, the hydrogen-ion concentration decreases tenfold.**

In the calculation of pH of solutions of strong acids, the $[H^+]$ is taken as equal to the concentration of the acid, which dissociates completely. But, in the cases of solutions of weak acids, where incomplete dissociation of the acids takes place, the $[H^+]$, and hence pH, can be calculated only if the degree of dissociation ($\alpha$) of the acid is known.

Let us consider the case of a weak acid, HA, present in a concentration of C gm-moles/litre, whose degree of dissociation is $\alpha$ at a particular temperature, say, 25°C.

$$\underset{C(1-\alpha)}{HA} \overset{\alpha}{\rightleftharpoons} \underset{C\alpha}{H^+} + \underset{C\alpha}{A^-} \quad \cdots \quad \cdots \quad (5.16)$$

$$\therefore\ [HA]=C(1-\alpha)\ ;\ [H^+]=C\alpha \text{ and } [A^-]=C\alpha$$

From eqn. 5.16,

$$K_a=\frac{[H^+][A^-]}{[HA]}$$ (where Ka is the *Acid dissociation constant of* HA.)

$$\text{or, } [H^+]=\frac{K_a[HA]}{[A^-]}=K_a\times\frac{[HA]}{[A^-]}$$

$$\therefore\ pH=-\log[H^+]=-\log K_a-\log\frac{[HA]}{[A^-]}$$

$$\text{or, } pH=pK_a+\log\frac{[A^-]}{[HA]} \quad \cdots \quad \cdots \quad (5.17)$$

(where $pK_a=-\log K_a$, defined by analogy with pH)

$$\text{or, } pH=pK_a+\log\frac{\alpha}{1-\alpha} \quad \cdots \quad \cdots \quad (5.18)$$

Hence, knowing pKa, which is a constant at any given temperature, and $\alpha$, the degree of dissociation of HA, the pH of any solution of a weak acid of a particular concentration at that temperature can be calculated. The equation (5.17) is known as the **Henderson equation** and it is used for the calculation of the pH of **buffer solutions** made by mixing requisite quantities of a weak acid and its salt.

If we consider a case when half of the weak acid, HA, undergoes dissociation, *i.e.* $\alpha = 0{\cdot}5$ (or 50%), then the Henderson eqn. becomes

$$\text{pH} = \text{pKa} + \log\frac{0{\cdot}5}{0{\cdot}5}\ ;\ \text{or,}\ \text{pH} = \text{pKa}$$

Thus, when half of the weak acid dissociates, the pH of the solution gives us the value of the pKa of that acid. Since $\text{pKa} = -\log \text{Ka}$, higher the value of pKa, lower is its strength as an acid. Thus, acetic acid with a pKa of 4·75 at 20°C is a weaker acid than formic acid whose pKa at 20°C is 3.

**pH of alkaline solutions.**

We know that alkaline solutions contain excess of hydroxyl ions and this may suggest that, since pH of a solution is a measure of its $[H^+]$, the concept of pH is not applicable to alkaline solutions. But, this is not so. We have previously arrived at the conclusion that, the ionic product of water is constant at a constant temperature, irrespective of whether the solution is acidic or alkaline, *i.e.* $[H^+][OH] = K_w$ is constant and is approximately equal to $1 \times 10^{-14}$ at 25°C. Thus, if the $[OH^-]$ of an aqueous solution increases, $[H^+]$ decreases and pH increases. Thus, higher the $[OH^-]$ (or lower the $[H^+]$) of an aqueous solution, higher is its pH. Let us consider an $\frac{N}{500}$ (*i.e.* $2 \times 10^{-3}$ M) solution of caustic soda. As NaOH is a strong base, it dissociates completely into $Na^+$ and $OH^-$ ions, and since one molecule of NaOH yields one $OH^-$ ion, the concentration of $OH^-$ ions is equal to that of NaOH. Thus, we have in this case,

$$[OH^-] = 2 \times 10^{-3} \text{ gm-ions/litre.}$$

We know, $K_W=[H^+][OH^-]=1\times10^{-14}$ at 25°C ;

$$\text{or,}\quad [H^+]=\frac{1\times10^{-14}}{[OH^-]}=\frac{1\times10^{-14}}{2\times10^{-3}}=5\times10^{-12}.$$

$$\therefore\quad pH=-\log(5\times10^{-12})$$
$$=11{\cdot}301.$$

Such problems can also be worked out in a different way. Taking the negative logarithm of both sides of eqn. 5.10, we have,

$$-\log[H^+]-\log[OH^-]=-\log K_W=-\log 10^{-14}$$

$$\text{or}\quad pH+pOH=pK_W=14 \quad \ldots\ \ldots \quad (5.19)$$

$$\therefore\quad pH+pOH=14 \text{ at } 25°C.$$

Thus, knowing either pH or pOH, the value of the other can be easily calculated.

Since pure water has a hydrogen-ion concentration of $10^{-7}$ gm-ions/litre, its pH=7. Acidic solutions have $[H^+]$ greater than $10^{-7}$ gm-ions/litre and hence, pH of an acid solution is always lower than 7. Similarly, the $[OH^-]$ of an alkaline solution is greater than $10^{-7}$ gm-ions/litre. As a result, the $[H^+]$ of alkaline solutions must be less than $10^{-7}$ gm-ions/litre, and to keep $K_W$ constant, pH of such alkaline solutions are always greater than 7. The relationship between pH, pOH, the $H^+$ and the $OH^-$ ion concentrations are given in Table 5.2.

We may now calculate the pH of a few acidic and alkaline solutions of known $[H^+]$ and $[OH^-]$.

(*a*) What is the pH of an $\frac{N}{600}$ solution of HCl ?

Since HCl is a strong acid, it is fully dissociated and as such, $[H^+]=\frac{1}{600}$ $=1{\cdot}66\times10^{-3}$ gm-ions per litre.

$$\therefore\quad pH=-\log(1{\cdot}66\times10^{-3})=2{\cdot}78.$$

(*b*) Calculate the pH of a solution of 0·0025 (M) HCl.

Since HCl is a strong acid and it is fully dissociated and thus, $[H^+]=2{\cdot}5\times10^{-3}$ gm-ions/litre in this case.

$$\therefore\quad pH=-\log(2{\cdot}5\times10^{-3})=2{\cdot}6021.$$

(*c*) Find out the pH of an $\frac{N}{5000}$ NaOH solution.

Since NaOH is a strong base which dissociates as $NaOH \rightleftharpoons Na^+ + OH^-$,
$[OH^-] = 2\times10^{-4}$ gm-ions/litre.
Since $[OH^-]\times[H^+] = K_w = 10^{-14}$

$$\therefore \quad [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{2\times10^{-4}} = 5\times10^{-11}$$

or, $pH = -\log[H^+] = -\log(5\times10^{-11})$
$= 10{\cdot}301.$

**Alternatively,** we know that, $pH + pOH = 14$ ; or, $pH = 14 - pOH$
Here $[OH^-] = 2\times10^{-4}$
$\therefore \quad pOH = -\log[OH^-] = -\log(2\times10^{-4}) = 3{\cdot}699$
So, $pH = 14 - 3{\cdot}699 = 10{\cdot}301$.

(*d*) What will be the $[H^+]$ of a solution whose pH is 2·5 ?
$pH = -\log[H^+]$
$\therefore \quad [H^+] = 10^{-pH}$
Here $pH = 2{\cdot}5$ ; so, $[H^+] = 10^{-2.5}$
or, $[H^+]$ = Antilog of $-2{\cdot}5$ = Antilog of $\bar{3}{\cdot}5 = 0{\cdot}3162\times10^{-2}$
Thus, this is a 0·003162 (N) solution with respect to $H^+$.

TABLE 5.6

| $[H^+]$ | $[OH^-]$ | pH | pOH | Chemical character |
|---|---|---|---|---|
| $10^{-1}$ | $10^{-13}$ | 1 | 13 | Acidic ↑ Acidity increases |
| $10^{-2}$ | $10^{-12}$ | 2 | 12 | |
| $10^{-3}$ | $10^{-11}$ | 3 | 11 | |
| $10^{-4}$ | $10^{-10}$ | 4 | 10 | |
| $10^{-5}$ | $10^{-9}$ | 5 | 9 | |
| $10^{-6}$ | $10^{-8}$ | 6 | 8 | |
| $10^{-7}$ | $10^{-7}$ | 7 | 7 | neutral |
| $10^{-8}$ | $10^{-6}$ | 8 | 6 | Alkaline ↓ Basicity increases |
| $10^{-9}$ | $10^{-5}$ | 9 | 5 | |
| $10^{-10}$ | $10^{-4}$ | 10 | 4 | |
| $10^{-11}$ | $10^{-3}$ | 11 | 3 | |
| $10^{-12}$ | $10^{-2}$ | 12 | 2 | |
| $10^{-13}$ | $10^{-1}$ | 13 | 1 | |
| $10^{-14}$ | $1(10^{0})$ | 14 | 0 | |

### Measurement of pH.

The important methods generally used to determine the pH of solutions fall into two different categories :

1. E.M.F. methods involving (a) hydrogen electrode, (b) quinhydrone electrode and (c) the glass electrode.

2. Indicator method involving acid-base indicators.

The most accurate method of determining the pH of a solution involves the measurement of e.m.f. of a cell comprising of two different half-cells or electrodes. The potential of one of these half-cells depends on the hydrogen-ion concentration of the solution used as the electrolyte and it is coupled with a standard half-cell or reference electrode of known electrode potential. The total e.m.f. of this assembly is then measured with the help of a potentiometer. Since the hydrogen electrode is considered to be the ultimate standard in the determination of pH, we will describe this method in some detail.

### Determination of pH by hydrogen electrode.

The solution *x*, whose pH is to be determined, is placed in a stoppered vessel of pyrex glass. A platinum-foil, coated with platinum black and welded to a stout platinum wire, is kept partly immersed in the experimental solution. A stream of pure hydrogen gas at 1 atmosphere pressure is bubbled through the solution, as a result of which both the solution and the platinised platinum electrode gets saturated with hydrogen and the following equilibrium is attained :

$$\tfrac{1}{2}H_2 \rightleftharpoons H^+ + e.$$

The whole system is illustrated in Fig. 5.1

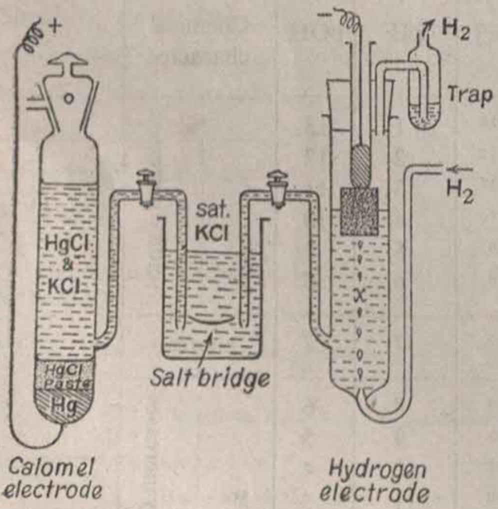


Fig. 5.1

Temperature of the whole system is kept constant by placing the apparatus in a thermostat. This half-cell thus behaves like a hydrogen electrode whose potential depends on the $[H^+]$ (or, more correctly, $a_{H^+}$) of the experimental solution. Thus, the expression for the electrode potential of this hydrogen electrode is

$$E_{H_2}=E^\circ_{H_2}-\frac{RT}{F}\ln[H^+]=-\frac{RT}{F}\ln[H^+]=-\frac{2\cdot303\ RT}{F}\log[H^+]$$

($E^\circ_{H_2}=0$, by convention, and F=one Faraday)

$$\text{or, } E_{H_2}=-0\cdot059\log[H^+]\quad(\text{at }25^\circ C)\quad\ldots\quad\ldots\quad(5.20)$$

This half-cell is now joined with a reference electrode like a **normal calomel electrode*** through a **salt-bridge** (saturated KCl solution containing agar-agar) to eliminate liquid-junction potential. After equilibrium is reached, the E.M.F. of the complete cell is measured. The total E.M.F. of the cell, E, is equal to the sum of the potentials of the two electrodes, *i.e.*

$$E=E_{ref}+E_{H_2}\quad\ldots\quad\ldots\quad(5.21)$$

where $E_{ref}$=potential of the standard calomel electrode. Thus, the expression for the E.M.F. of the cell is, $E=E_{ref}-0\cdot059\log[H^+]$

$$\text{or, } pH=\frac{E-E_{ref}}{0\cdot059}\quad\ldots\quad\ldots\quad(5.22)$$

So, pH of the solution can be computed by measuring the E.M.F. of the combined cell.

**Limitation of the hydrogen electrode method.**

(i) If the solution contains an oxidising agent, this method cannot be used.

(ii) The method is not applicable if the solution contains ions of noble metals like Cu, Ag, Au *etc.*

(iii) In presence of unsaturated compounds, this method does not give correct results.

**Determination of pH by glass electrode.****

The glass electrode is most widely used in the determination of pH. It has been found that, if a thin glass-membrane separates two solutions differing in hydrogen-ion concentration, a potential ($E_G$) is developed across the membrane, which depends on the hydrogen-ion concentrations of the solutions. If one solution is kept fixed, then the electrode potential depends on the $[H^+]$ of the other, and is given by

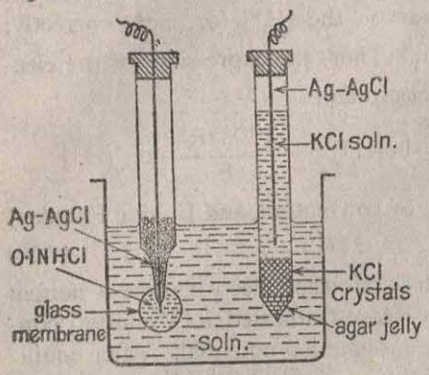
---

*Will be discussed in details in the next chapter.

**A glass electrode is made up of a small glass globe of a thin special glass membrane in which a silver-silver chloride electrode is dipped. The globe generally contains a solution of a dil. HCl.

$$E_G = E^\circ_G - \frac{RT}{F}\ln [H^+]$$

$$= E^\circ_G - 0{\cdot}059 \log [H^+] \qquad .. \quad (5.23)$$



Glass electrode

Fig. 5.2

The glass electrode is dipped into the experimental solution and allowed to attain equilibrium with the hydrogen ions in the experimental solution. It is then coupled with a standard Ag-AgCl electrode or a standard calomel electrode and the total E.M.F. (E) is measured potentiometrically.

$$E = E_G - E_{Ag\text{-}AgCl} = E^\circ_G - 0{\cdot}059 \log [H^+] - E_{Ag\text{-}AgCl}$$

$$\text{or, } E = E^\circ_G + 0{\cdot}059\ pH - E_{Ag\text{-}AgCl} \qquad .. \qquad .. \qquad (5.24)$$

Thus, pH can be calculated by measuring E.

In actual practice, the standard calomel electrode is used most widely and the glass electrode-calomel electrode assembly is used at first with a buffer solution of accurately known pH. Let the pH of that buffer solution be $(pH)_1$, and the E.M.F. of the assembly with that buffer be $E_1$. The solution of unknown pH is then substituted for the buffer and the E.M.F. of the cell is again measured. Let it be $E_2$ and let the unknown pH value be $(pH)_2$.

Now, we can write,

$$\Delta E = (E_1\text{-}E_2) = 0{\cdot}059\ [(pH)_1 - (pH)_2] \qquad .. \qquad (5.25)$$

From this eqn., $(pH)_2$ can be easily found out.

**Hydrolysis of salts.**

The process of interaction of the ions of a salt with water, resulting in a partial reversal of neutralisation, is called hydrolysis. As a result of this phenomenon, aqueous solutions of many neutral salts often react acidic or alkaline. Thus, an aqueous solution of $NH_4Cl$ reacts acidic, while that of sodium acetate is alkaline in character.

A neutral salt BA is formed by the neutralisation of the acid HA and the base BOH,

$$HA+BOH \rightleftharpoons BA+H_2O.$$

This salt ionises in water as : $BA \rightleftharpoons B^+ + A^-$.

The cation $B^+$ or the anion $A^-$, or both may now react with water and undergo hydrolysis. Three different types of salts which undergo hydrolysis to different extents may be recognised :

1. Salts of strong acid and weak base,
2. Salts of strong base and weak acid,
3. Salts of weak acid and weak base.

[It is to be remembered that the salts being strong electrolytes are considered to be fully ionised in solution.] We will now consider the different cases of salt-hydrolysis in details.

### 1. Salts of strong acid and weak base.

Let BA represent the salt of a strong acid HA and a weak base BOH and it fully ionises in solution as

$$BA \rightleftharpoons B^+ + A^-.$$

We will now consider the character of $B^+$ and $A^-$ in the light of conjugate acid-base pair relationship of Bronsted's protonic concept. Since HA is a strong acid, its conjugate base $A^-$ is a weak base and hence is not a good proton-acceptor. It will not be able to accept protons from the water molecule and will not be able to generate $OH^-$ ions. But, the conjugate acid $B^+$ of the weak base BOH is strong and will accept $OH^-$ ions from water molecule :

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

at equilibrium : $C(1-x)$ $\quad Cx \quad Cx$ ($x$ = degree of hydrolysis)

Since BOH is a weak base, it will not dissociate appreciably; but the proton generated in the solution by the above reaction will make the solution acidic. Thus, due to hydrolysis, the aqueous solution of a salt of strong acid and weak base will react acidic, *i.e.* all of them will have $pH < 7$. Ammonium salts of all the mineral acids and the mineral acid salts of most of the organic bases are good examples of such cases.

Now we will consider the quantitative aspects of this class of hydrolysis. The equilibrium constant of the above reaction is given

by $K_h = \dfrac{a_{BOH} \times a_{H^+}}{a_{B^+} \times a_{H_2O}} = \dfrac{a_{BOH} \times a_{H^+}}{a_{B^+}}$ $(a_{H_2O} = 1)$

In dilute solutions, the activity-terms ($a$'s) may be replaced by the molar concentration terms (C's) and the above equation may be written as

$$K_h = \frac{C_{BOH} \times C_{H^+}}{C_{B^+}} \quad \cdots \quad (5.26)$$

If $x$ represents the degree of hydrolysis and C is the concentration of the salt AB, then $K_h = \frac{Cx^2}{1-x}$ .. .. (5.27)

Thus, $K_h$ can be calculated if $x$ is known. Under the conditions when $x$ is small, we can take $(1-x) \simeq 1$ and $K_h \simeq Cx^2$.

$$\text{or, } x = \sqrt{\frac{K_h}{C}} \quad \cdots \quad (5.28)$$

Thus, if $K_h$ is known, $x$ can be calculated. It is to be noted also that, $x \propto \frac{1}{\sqrt{C}}$

We have already seen that, $K_h = \frac{C_{BOH} \times C_{H^+}}{C_{B^+}}$

Multiplying both the numerator and the denominator by $C_{OH^-}$, we get, $K_h = \frac{C_{BOH} \times C_{OH^-} \times C_{H^+}}{C_{OH^-} \times C_{B^+}}$

But, $K_b = \frac{C_{B^+} \times C_{OH^-}}{C_{BOH}}$ and $C_{H^+} \times C_{OH^-} = K_w$

$$\therefore \quad K_h = \frac{K_w}{K_b} \quad \cdots \quad (5.29)$$

$$\text{Thus, } x = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b . C}} \quad \cdots \quad (5.30)$$

Since the degree of hydrolysis is $x$, from the reaction representing the hydrolysis of the species $B^+$, we get,

$$C_{H^+} = Cx. \quad \therefore \quad pH = -\log Cx = -\log \left( C \times \sqrt{\frac{K_w}{K_b . C}} \right)$$

$$\text{or, } pH = -\log \left( \sqrt{\frac{K_w C}{K_b}} \right)$$

$$= -\tfrac{1}{2} \log K_w - \tfrac{1}{2} \log C + \tfrac{1}{2} \log K_b$$

$$= \tfrac{1}{2} pK_w - \tfrac{1}{2} pK_b - \tfrac{1}{2} \log C \; (\because -\log K_w = pK_w; -\log K_b = pK_b)$$

$$\text{or, } pH = 7 - \tfrac{1}{2} pK_b - \tfrac{1}{2} \log C \quad \cdots \quad (5.31)$$

**Application to practical problems.**

(*a*) Calculate the pH of an $\frac{M}{200}$ solution of $NH_4NO_3$, given : $K_{NH_4OH}=1{\cdot}8\times10^{-5}$ (Kb). $[NH_4^+]=\frac{1}{200}$ M$=0{\cdot}005$ M
$pK_b=-\log K_b=-\log 1{\cdot}8\times10^{-5}=4{\cdot}74$.

According to eqn. (5.31), $pH = 7-\frac{4{\cdot}74}{2}-\frac{1}{2}\log 0{\cdot}005=5{\cdot}7805$.

### 2. Salts of strong base and weak acid.

If the salt is BA, it ionises in solution as

$$\begin{array}{ccc} BA & \overset{x}{\rightleftharpoons} & B^+ + A^- \\ C(1-x) & & Cx \quad Cx \end{array}$$

Here, due to reasons discussed in the previous case, $A^-$ is a strong base and $B^+$ is a weak acid. Thus, $A^-$ will accept protons from $H_2O$ molecules, leaving behind the residual $OH^-$ ions, and the solution will react alkaline, *i.e.* it will have pH>7.

Since it is the $A^-$ ion which will undergo hydrolysis, the hydrolytic equilibrium may be written as : $A^-+H_2O \rightleftharpoons HA+OH^-$,

or, $K_h = \frac{a_{HA}\times a_{OH^-}}{a_{A^-}\times a_{H_2O}} = \frac{a_{HA}\times a_{OH^-}}{a_{A^-}}$ (as $a_{H_2O}=1$).

In dilute solution, $$K_h = \frac{C_{HA}\times C_{OH^-}}{C} = \frac{Cx^2}{(1-x)} \quad .. \quad (5.32)$$

When $x$ is small, $K_h=Cx^2$; or, $$x=\sqrt{\frac{K_h}{C}} \quad .. \quad .. \quad (5.33)$$

We can also write, $$K_h = \frac{C_{HA}\times C_{OH^-}\times C_{H^+}}{C_{A^-}\times C_{H^+}}$$

$$=\frac{K_w}{K_a}\left[\text{Since } K_a=\frac{C_{H^+}\times C_{A^-}}{C_{HA}}\right] \quad .. \quad (5.34)$$

$$\therefore\ x=\sqrt{\frac{K_w}{K_a.C}} \quad .. \quad .. \quad (5.35)$$

and $$Cx = \sqrt{\frac{K_w.C}{K_a}} = C_{OH^-} \text{ (since } C_{OH^-}=Cx) \quad .. \quad (5.36)$$

Since $C_{H^+}=\frac{K_w}{C_{OH^-}}$ and $C_{OH^-}=\sqrt{\frac{K_w.C}{K_a}}$

$$\therefore\ C_{H^+}=K_w \div \sqrt{\frac{K_w.C}{K_a}}=\sqrt{\frac{K_wK_a}{C}} \quad .. \quad (5.37)$$

$$\text{or, } pH=-\log C_{H^+}=-\log\left[\sqrt{\frac{K_w.K_a}{C}}\right]$$

$$=\tfrac{1}{2}\,pK_w+\tfrac{1}{2}\,pK_a+\tfrac{1}{2}\log C$$

$$=7+\tfrac{1}{2}\,pK_a+\tfrac{1}{2}\log C.$$

**Application to practical problems.**

(*a*) Calculate the pH of a solution of $2{\cdot}5\times10^{-2}$ molar sodium acetate. Given pKa of acetic acid=4·74 at 25°C.

Here $C=2{\cdot}5\times10^{-2}$, $\tfrac{1}{2}\,pK_a=\frac{4{\cdot}74}{2}=2{\cdot}37$

$$\therefore\ pH=7+2{\cdot}37+\tfrac{1}{2}\log(2{\cdot}5\times10^{-2})$$
$$=9{\cdot}37-1{\cdot}301$$
$$=8{\cdot}069.$$

**3. Salts of weak acid and weak base.**

Here both the ions will undergo hydrolysis, but the products would remain almost undissociated, as both of them are weak. The hydrolytic equilibrium may be represented as :

$$\underset{C(1-x)}{B^+} + \underset{C(1-x)}{A^-} + H_2O \rightleftharpoons \underset{Cx}{BOH}+\underset{Cx}{HA}$$

∴ The hydrolysis constant can be finally written as,

$$K_h = \frac{C_{BOH}\times C_{HA}}{C_{B^+}\times C_{A^-}}$$

Multiplying the numerator and the denominator by $C_{H^+}\times C_{OH^-}$,

$$\text{we get, } K_h = \frac{C_{BOH}}{C_{B^+}\times C_{OH^-}}\times\frac{C_{HA}}{C_{A^-}\times C_{H^+}}\times C_{H^+}\times C_{OH^-}$$

$$\text{or, } K_h = \frac{1}{K_b}\times\frac{1}{K_a}\times K_w$$

$$\text{or, } K_h = \frac{K_w}{K_a.K_b} \quad .. \quad .. \quad (5.38)$$

Again, if $x$ be the degree of hydrolysis and C be the concentration of the salt, then,

$$K_h = \frac{x^2}{(1-x)^2} \quad \therefore\ \sqrt{K_h} = \frac{x}{(1-x)} \quad .. \quad .. \quad (5.39)$$

Thus, in this case, the degree of hydrolysis and the pH of the solution is independent of concentration of the salt.

We also know that, $K_a = \dfrac{C_{H^+} \times C_{A^-}}{C_{HA}}$

or, $C_{H^+} = \dfrac{K_a \times C_{HA}}{C_{A^-}}$.

Since $C_{HA} = Cx$ and $C_{A^-} = C(1-x)$, $\therefore\ C_{H^+} = K_a \times \dfrac{x}{(1-x)} = K^a\sqrt{}\times K^h$

Also $K_h = \dfrac{K_w}{K_aK_b}$. $\therefore\ C_{H^+} = K_a \times \sqrt{\dfrac{K_w}{K_aK_b}} = \sqrt{\dfrac{K_w.K_a}{K_b}}$

$$\therefore\ pH = -\log\sqrt{\frac{K_w.K_a}{K_b}} \qquad .. \qquad (5.40)$$

$$= \tfrac{1}{2}\,pK_w + \tfrac{1}{2}\,pK_a - \tfrac{1}{2}\,pK_b.$$

$$= 7 + \tfrac{1}{2}\,pK_a - \tfrac{1}{2}\,pK_b. \qquad .. \qquad (5.41)$$

Three different cases may be considered here.

(*a*) $pK_a = pK_b$, *i.e.* the values of the dissociation constant of the acid and the base are equal. Then, $pH = 7{\cdot}0$, *i.e.* the solution is neutral.

(*b*) $K_a > K_b$, *i.e.* the acid is stronger. Then $pK_a < pK_b$

$\therefore\ pH < 7{\cdot}0$, *i.e.* the solution is acidic.

(*c*) $K_b > K_a$, *i.e.* $pK_b < pK_a$. The base is stronger and hence, $pH > 7$.

## BUFFER SOLUTIONS.

We have already noted that pure water has a pH=7. If 0·1 ml. of (N)HCl (or any strong acid) is added to one litre of pure water, its pH becomes 4. Again, the addition of 0·1 ml. of (N) NaOH (or any strong base) to one litre of water, raises the pH value to 10. It may be concluded that water do not have much capacity of resisting the change of its pH when addition of even small quantities of acids or bases is made. But, if 0·1 ml. of (N) HCl or 0·1 ml. of (N) NaOH is added to one litre of ammonium acetate solution, the pH remains practically constant at 7·0. The pH of ammonium acetate soln. (a salt of weak acid and weak base) is approximately 7, as both acetic acid and ammonium hydroxide have nearly the same value of $K_a$ and $K_b$. **Solutions,** like ammonium acetate, **which has some reserve capacity for resisting the change of hydrogen ion concentration by the addition of small amounts of acids or bases, are known as buffer solutions.** The process by which a buffer solution neutralises the $H^+$ ions or $OH^-$ ions added from outside, is called **buffer action.**

## BUFFER CAPACITY.

The buffer capacity of a solution is defined by $\dfrac{d_B}{d\mathrm{pH}}$, where

$d$pH is the increase of the pH of the buffer solution that is caused from the addition of $d_B$ amount of base. Addition of acid which decreases the pH, is equivalent to a negative amount of base. This is generally designated by $\beta$. The greater the buffer capacity, the larger the amount of acid or alkali which must be added to produce a definite change of pH. So, the *buffer capacity* is a *quantitative measure* of the buffering ability of a solution.

## COMPOSITION OF BUFFER SOLUTIONS.

Buffer solutions are made up of a mixture of (i) a weak acid and its salt (e.g. $CH_3COOH$ and $CH_3COONa$), (ii) a weak base and its salt (.e.g. $NH_4OH$ and $NH_4Cl$), (iii) the salt of a weak acid and weak base (e.g. $CH_3COONH_4$) and (iv) mixture of salts of polybasic acids (e.g. $NaH_2PO_4$ and $Na_2HPO_4$).

We will now explain the mechanism of buffer action, taking two buffer solutions frequently used in inorganic analysis. It may be pointed out at the onset that, the **common ion effect** plays an important role in buffer action.

## ACIDIC BUFFERS.

First of all, we consider the case of the acetate buffer solution which consists of acetic acid and sodium acetate solutions. The pH of such solutions generally lie in the range 3·7—5·6, and hence they are acidic buffers.

Sodium acetate, being a salt, ionises almost completely as, $CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$, furnishing a considerable amount of $CH_3COO^-$ ion, depending upon the concentration of $CH_3COONa$. Acetic acid being a weak acid, is very little dissociated in solution in presence of sodium acetate due to common ion effect, the common ion being the $CH_3COO^-$ ion. Thus, this buffer solution consists essentially of $CH_3COOH$, $CH_3COO^-$ and $Na^+$ species.

When a strong acid like HCl is added from outside to this buffer solution, it dissociates fully as $HCl \rightleftharpoons H^+ + Cl^-$. As soon as the $H^+$ ions are produced, the acetate ions in the buffer solution (which is the strong conjugate base of the weak acetic acid) react with them, $CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$, forming acetic acid which is weak and does not dissociate in presence of sodium acetate existing in the buffer. In this manner, this buffer solution neutralises the added $H^+$ ion and keeps the pH constant.

When a strong base, say NaOH, is added, the $OH^-$ ions produced are acted upon by the undissociated acetic acid present in the buffer, $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$, with the production of water and more acetate ions. Thus, the $OH^-$ ions added from outside are neutralised and the pH of the solution is kept constant. This acetate buffer is generally used in inorganic qualitative analysis for the separation of phosphate before proceeding beyond group IIIA. Buffer solution of pH ranging from 4—6 are generally prepared by mixing requisite quantities of acetic acid and sodium acetate.

**Calculation of pH of buffer solutions made up of a weak acid and its salt : Application of Henderson Equation.**

The Henderson equation is

$$pH = pKa + \log \frac{[\text{Anion of the acid}]}{[\text{Undissociated acid}]}.$$

Here, the concentration of the salt is the concentration of the anion of the acid,

*i.e.*, [anion of the acid] = [Salt] = $[CH_3COONa]$ (say).

Let this be $C_1$ moles/litre.

Let the concentration of the weak acid (acetic acid) be $C_2$ moles/litre.

$$\therefore \quad pH = pKa + \log \frac{[\text{Salt}]}{[\text{Acid}]} = pKa + \log \frac{C_1}{C_2} \quad .. \quad (5.42)$$

For a buffer solution, when [Salt] = [Acid], then pH = pKa. Thus, if equimolar solutions of an acid and its salt are used, we obtain a buffer whose pH is equal to the pKa of the acid. When the ratio [salt]/[acid] is varied, the buffer solution will have a different pH, but not far away from the value of pKa. The maximum variation in the [salt]/[acid] ratio, which is generally allowed, is 1 : 10 or 10 : 1. The limiting values of the buffer pH in those cases are,

$$pH = pKa + \log \frac{1}{10} = pKa - 1 \text{ and } pH = pKa + \log 10 = pKa + 1.$$

Thus, the pH range through which a buffer can act efficiently is $pKa \pm 1$, *i.e.* between two units of pH centred round the pKa of the acid.

**Practical application.**

(*a*) Find out the pH of a buffer solution made by mixing 10 ml of 0·1 (N) acetic acid and 10 ml 0·2N sodium acetate. Given, Ka of acetic acid $= 1{\cdot}8 \times 10^{-5}$ at 25°C.

Here, total volume of the buffer = 10 ml + 10 ml = 20ml.

$$\therefore \text{ Concn. of sodium acetate, } [CH_3COONa] = \frac{0{\cdot}2 \times 10}{20} \text{ (N)}$$

and ,, ,, acetic acid, $[CH_3COOH] = \dfrac{0{\cdot}1 \times 10}{20}$ (N)

$$\therefore \quad \frac{[\text{Salt}]}{[\text{Acid}]}=\frac{0{\cdot}1}{0{\cdot}05}=2.$$

Also, $pKa=-\log 1{\cdot}8\times10^{-5}=4{\cdot}74$.

So, $pH=pKa+\log\frac{[\text{Salt}]}{[\text{Acid}]}=4{\cdot}74+\log 2=4{\cdot}74+0{\cdot}3010=5{\cdot}0410$.

## BASIC BUFFERS.

**A buffer solution made up of ammonium hydroxide and ammonium chloride** (pH range 8·5—10, and hence it is basic in character).

In this buffer, ammonium chloride dissociates completely as,

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-.$$

The dissociation of $NH_4OH$ is much depressed by the common ion effect involving the common ion, $NH_4^+$. Thus, this buffer contains the $NH_4^+$, $NH_4OH$ and $Cl^-$ species.

When a strong acid like HCl is added from outside, it dissociates as, $HCl \rightleftharpoons H^+ + Cl^-$. The $NH_4OH$ molecules at once react with the hydrogen ions: $NH_4OH+H^+ \rightleftharpoons NH_4^+ + H_2O$ and thus neutralise them.

When a strong base, such as NaOH, is added, $NH_4^+$ ions (strong conjugate acid of the weak base $NH_4OH$) present, immediately react as, $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$, and neutralise them. In this manner, this buffer resists the change of pH by the addition of acid or alkali and keeps the pH constant. This buffer is used for the selective precipitation of the hydroxides of the Gr.IIIA (of analytical chemistry) metals without precipitating the Gr. IIIB hydroxides and magnesium hydroxide. Buffer solutions of pH greater than 7 (generally between pH 8—10) are prepared by mixing the requisite amounts of $NH_4OH$ and $NH_4Cl$. For such a buffer, made up of a weak base and its salt,

$$pOH=pKb+\log\frac{[\text{Salt}]}{[\text{base}]} \quad .. \quad .. \quad (5.43)$$

and such buffers can operate efficiently in the pOH range $pKb\pm1$.

We know that, $pH+pOH=14$ ; or, $pH=14-pOH$

$$\therefore \quad pH \text{ (of the basic buffer)}=14-pKb-\log\frac{[\text{Salt}]}{[\text{base}]}$$

$$=14-pKb+\log\frac{[\text{base}]}{[\text{Salt}]}.$$

## NEUTRAL BUFFER.

A neutral buffer in the pH 7 range is prepared by mixing solutions of $NaH_2PO_4$ and $Na_2HPO_4$. Here $NaH_2PO_4$ acts as the weak acid ($Ka=6{\cdot}2\times10^{-8}$) and $Na_2HPO_4$ as its salt. The following equilibrium exists in solution : $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$.

So, when $[H_2PO_4^-]=[HPO_4^{2-}]$, the pH of the buffer is the same as the pKa of the acid, $H_2PO_4^-$.

Blood and other physiological fluids are buffered. Blood is buffered at pH$\sim$7·4, so that the pH of blood changes very little from its normal value on addition of small amounts of acid or base. The important buffering components in blood are the serum proteins which contain both basic and acidic groups and these can combine with the small amounts of the added acids or bases so that the pH remains virtually constant.

### UNIVERSAL BUFFER.

As already known, the effective buffer range for a weak acid or a weak base is approximately from pH=pKa+1 to pH=pKa−1. When two or more buffers are present in a system, the effects are additive, so that the buffering ability of a mixture is spread over a wider range of pH. If a buffer system has several successive pKa values which differ by about 2 pH units, approximately linear buffer capacity results. This property has been exploited in 'universal' buffers, having high buffer capacities over a wide pH range. A mixture of citric acid, $KH_2PO_4$, boric acid and diethyl barbituric acid, in conjunction with NaOH, has been used to prepare a buffer that can efficiently work in the pH range 2·6−12·0.

Table 5.7 enlists some more common buffers along with their pH ranges.

TABLE 5.7

| Buffer solutions | pH range |
|---|---|
| Phthalic acid+Potassium hydrogen phthalate | 2·2 — 3·8 |
| Acetic acid+sodium acetate | 3·7 — 5·6 |
| $NaH_2PO_4+Na_2HPO_4$ | 4·0 — 6·2 |
| Boric acid+borax | 5·9 — 8·0 |
| $NH_4Cl+NH_4OH$ | 8·5 — 10·8 |
| Borax+NaOH | 9·2 — 11·0 |
| Glycine+NaOH | 8·5 — 13·0 |

## INDICATORS.

Indicators are materials which indicate the end-points of titrimetric processes by characteristic colour changes. Three different types of indicators are commonly used to detect the equivalence or end-points of different types of titrations. These are : (i) **Acid-base indicators,** which detect the end-points of acid-base reactions by a suitable change of colour at that point. (ii) **Red-ox indicators** are used in the determination of equivalence-point of oxidation-reduction reactions. They will be dealt with in the next chapter. (iii) **Adsorption indicators** indicate the end-points of precipitation reactions.

At present we propose to deal with the acid-base indicators. Acid-base indicators are generally weak organic acids or weak organic bases. In solution, the indicator molecule is involved in the equilibrium :

$$\underset{\text{acid colour}}{\mathrm{HIn}} \rightleftharpoons \underset{\text{alkaline colour}}{\mathrm{H^+ + In^-}}$$

The undissociated form of the indicator, HIn, has a colour different from that of the dissociated form, $In^-$. When the solution is acidic, the ionisation, indicated above, is very much suppressed due to common ion effect by the presence of a large amount of $H^+$. The colour of the solution under this condition is due exclusively to the HIn species and is called the *acid colour*. In alkaline solution, the concentration of $In^-$ predominates and the solution assumes the colour of the $In^-$ species, which is the *alkaline colour* of the indicator.

The ionisation constant of the indicator, HIn, is given by,

$$K_{In} = \frac{[In^-][H^+]}{[HIn]}, \text{ where } K_{In} = \text{indicator constant,}$$

$$\text{or } [H^+] = \frac{K_{In}\,[HIn]}{[In^-]},$$

$$\text{or, } pH = -\log K_{In} - \log\frac{[HIn]}{[In^-]}$$

$$\text{or, } pH = pK_{In} + \log\frac{[In^-]}{[HIn]} \quad .. \quad .. \quad (5.44)$$

This is nothing but the Henderson equation, with which we are already familiar.

When the indicator is 50% ionized, *i.e.*, when $[HIn]=[In^-]$, $pH=pK_{In}$.

So, the indicator constant, $K_{In}$, is the value of the hydrogen-ion concentration at which the change in colour of the indicator is half completed.

Since, dissociation constant, $K_{In}$, and hence $pK_{In}$ of an indicator is a characteristic and specific property of that indicator, the pH at which the indicator shows its neutral colour will be different for different indicators.

Equation 5.44 can be written as,

$$pH = pK_{In} + \log \frac{[\text{Ionised form with alkaline colour}]}{[\text{Unionised form with acidic colour}]}.$$

From this equation, it is evident that at different pH values of the solution, the indicator exists in a definite ratio of the ionised and the unionised forms. Both the forms exist in any pH, but the human eye can distinguish one colour from the other, only when the form of indicator responsible for that colour predominates. It has been found experimentally that the acid colour (the colour of HIn) is clearly perceived when $\frac{[HIn]}{[In^-]} \geqslant 10$

This, naturally happens when

$pH = pK_{In} - 1$ (by putting $\frac{[HIn]}{[In^-]} = 10$ in eqn. 5·44)

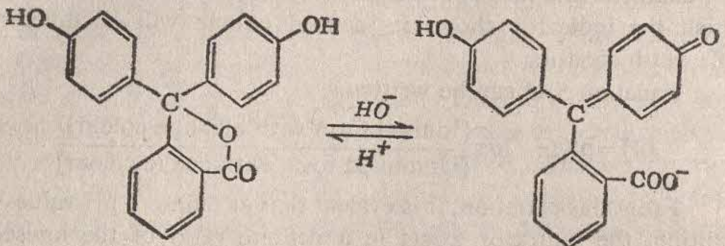
Similarly, the alkaline colour is clearly detected when

$\frac{[In^-]}{[HIn]} \geqslant 10$, *i.e.* at $pH = pK_{In} + 1$.

When an acid is being titrated with a base, the indicator used will appear to change from acid colour to the alkaline colour within the pH range $pK_{In} - 1$ to $pK_{In} + 1$, *i.e.*, within two units of pH centering the $pK_{In}$ value. This pH-range is known as the *colour change interval* of an indicator. Thus, methyl red, which has a $pK_{In}$ 5.1, changes from acid (red) to alkaline (yellow) colour in the pH range 4.2—6.3.

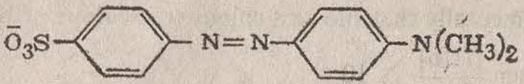
The colour-changes of the acid-base indicators during titration are due to certain structural changes in the molecules of the indicators. As already said, the acid-base indicators are generally very weak organic acids or bases. Each of them are capable of existing in two tautomeric forms. One of the tautomers exists in the non-electrolyte form and does not ionise ; but, the other form is an electrolyte and hence ionises in solution. The colours of the two tautomeric forms are different. The colour of the ion ($In^-$) formed is the same as that of the tautomer from which it is produced. This is illustrated by taking examples of two important acid-base indicators, *viz.* phenolphthalein and methyl orange, which will help in understanding the phenomenon of the colour-change.

1. *Phenolphthalein.*

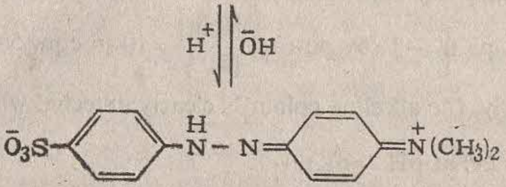


[Acid colour (HIn) : Colourless] [Alkaline colour (In⁻) : Deep Red]

2. *Methyl orange.*



[Alkaline colour (In⁻) : Orange]



[Acid colour (HIn) : Pinkish Red]

Some of the more commonly used acid-base indicators, with their pKIn values and the pH-ranges for their colour-change are given below in Table 5.8.

TABLE 5.8

| Indicator | pKIn | Change of colour |  | pH range |
|---|---|---|---|---|
|  |  | acid | alkali |  |
| Methyl orange | 3·7 | red | yellow | 3·1— 4·4 |
| Bromocresol green | 4·7 | yellow | blue | 3·8— 5·4 |
| Methyl red | 5·1 | red | yellow | 4·2— 6·3 |
| Chlorophenol red | 6·0 | yellow | red | 4·8— 6·4 |
| Bromothymol blue | 7·0 | yellow | blue | 6·0— 7·6 |
| Phenol red | 7·9 | yellow | red | 6·8— 8·4 |
| Phenolphthalein | 9·6 | colourless | red | 8·3—10·0 |
| Thymolphthalein | 9·2 | colourless | blue | 8·3—10·5 |

## CHOICE OF INDICATORS.

When acids and bases react in equivalent amounts, salts are produced. During the consideration of the phenomenon of hydrolysis, we have seen that the salt of a strong acid and a strong base does not suffer hydrolysis and the pH of the end-point is 7. But, before the end-point is reached, when 99·9% of the acid is neutralised, the pH is 4·0, and after the end-point, the addition of 0·1% base raises the pH to 10·0, and at the end-point, the pH is just 7. Thus, the pH changes very sharply near the end-point from 4 to 10 and any indicator, whose colour-change interval lies within this range, can be used. Table 5.9 contains a set of data of titration of 100 ml. 0·1 HCl with 0·1 (N) NaOH.

TABLE 5.9

| ml. of 0·1(N)NaOH added | % of HCl unneutralised | $[H^+]$ | pH |
|---|---|---|---|
| 0 | 100 | $10^{-1}$ | 1·0 |
| 50 | 50 | $5\times10^{-2}$ | 1·3 |
| 99·9 | 0·1 | $10^{-4}$ | 4·0 |
| 100·0 | 0 | $10^{-7}$ | 7·0 |
| 100·1 | excess alkali | $10^{-10}$ | 10·0 |

When, to a weak acid solution (acetic acid), an equivalent amount of a strong base (caustic soda) is added, the salt formed suffers hydrolysis and reacts alkaline, *i.e.*, the pH at equivalence-point is greater than 7. Thus, an indicator like phenolphthalein or thymolphthalein (vide Table 5.8) can be used.

In the titration of a strong acid by a weak base (HCl vs $Na_2CO_3$ or $NH_4OH$), the salt formed at the equivalence-point undergoes hydrolysis and react acidic, *i.e.* the pH at the equivalence-point is $<7$. Hence, in this case, indicators like methyl orange or methyl red, whose colour-change interval lies in the acidic region (vide Table 5.8) should be used.

The principle underlying the choice of indicator can be more clearly appreciated if we examine the titration curves of the different types of acids and bases which are shown below in Fig. 5.3.

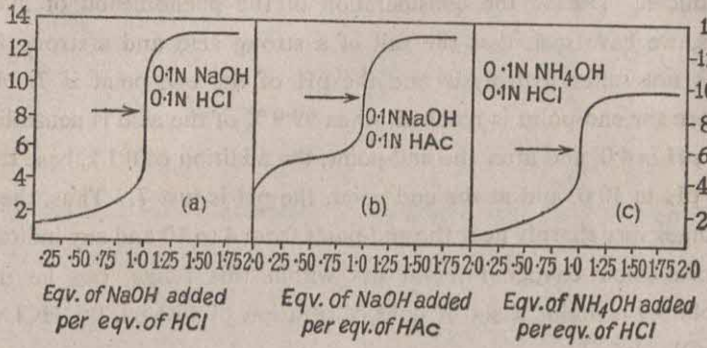


Fig. 5.3

**Titration of a strong acid with a strong base.**

When a strong acid like HCl (say, 0·1N) is titrated with a strong base like NaOH (say, 0·1N), the type of curve obtained is shown in fig. 5·3(a). It is evident from the curve that, in the immediate vicinity of the equivalence-point, the pH jumps very sharply from 4 to 10. Hence, any indicator with a colour-change range within this pH interval is suitable for detecting the end-point of such titrations.

**Titration of a weak acid (acetic acid, 0·1N) with a strong base (NaOH, 0·1N).**

When a 0·1N acetic acid is titrated with a 0·1N caustic soda, the curve shown in fig. 5.3 (b) is obtained. As the salt formed (sodium acetate) suffers hydrolysis, the pH changes rather sharply from 7—10 at the equivalence-point and hence, an indicator like phenolphthalein (colour-change interval 8·3—10), which changes its colour within this pH range should be used.

**Titration of a strong acid (0·1N HCl) by a weak base (0·1N $NH_4OH$).**

The curve representing the titration of 0·1N HCl with 0·1N $NH_4OH$ is represented in fig 5.3 (c). It is clear from the figure that, when the equivalence-point is reached, the pH rises rather steeply from 4—7. Indicators like methyl red (colour-change interval 4·2—6·3), whose colour change-interval lie in this pH region, are suitable for such titrations.

**Titration of a weak acid (0·1N acetic acid) by a weak base (0·1N $NH_4OH$).**

Such titrations do not generally give any meaningful results, and as such, they should not be attempted.

*Soft and Hard Acids and Bases* (*The* SHAB *concept*)*

In 1958 Ahrland, Chatt and Davis reviewed the phenomenon of acid-base or donor-acceptor interaction in the light of the Lewis concept and pointed out that the metal ion acceptors (Lewis acids) can be conveniently classified into two general categories. *Class* (*a*) *acceptors* consist of the metal ions which form most stable complexes with ligands in which the donor atoms are the first member of each of the non-metal groups (Grs VB, VIB and VIIB) of the periodic table. *Class* (*b*) *acceptors* are metal ions for which stable complexes are formed when the donor atoms are the heavier members of the non-metal groups (VB, VIB and VIIB) mentioned before. It is well-known that various molecules and ions containing atoms of VB (N, P, As), VIB (O, S, Se) and VIIB (F, Cl, Br, I) elements possess powerful donor properties because of the presence of one or more lone-pair of electrons in their valence-shells. $NH_3$, $NR_3$, $PR_3$, $AsR_3$ ; $H_2O$, $R_2S$, RHS, $R_1R_2C{=}S$, $R_2Se$, $R_1R_2C{=}Se$ ; $F^-$, $Cl^-$, $Br^-$, $I^-$ etc. are well-known examples of such donors. Stabilities** of the complexes of the *class* (*a*) and *class* (*b*) metals with ligands containing the above-mentioned donor atoms exhibit the trend shown in the following table.

TABLE 5.10

| Acceptor class (with examples) | Periodic groups to which the donor atom belongs | Gradation of stability of the donor-acceptor complexes |
|---|---|---|
| Class (a) metal ions<br>[$Li^+$, $Na^+$, $Be^{+2}$, $Mg^{+2}$, $Mn^{+2}$, $Al^{+3}$, $Cr^{+3}$, $Co^{+3}$, $Fe^{+3}$ etc.] | Gr VB<br>Gr VIB<br>Gr VIIB | $N \gg P > As$<br>$O \gg S > Se$<br>$F \gg Cl < Br > I$ |
| Class (b) metal ions<br>[$Cu^{+1}$, $Ag^{+1}$, $Hg^{+1}$, $Pd^{+2}$, $Cd^{+2}$, $Hg^{+2}$, $M^0$ (metal atoms) etc.] | Gr VB<br>Gr VIB<br>Gr VIIB | $N \ll P > As$<br>$O \ll S \sim Se$<br>$F < Cl < Br < I$ |

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*Students are advised to go through the chapter on coordination compounds before reading the SHAB concept.

**See the chapter on coordination chemistry.

Careful scrutiny of the above classification reveals the following facts :

(A) The *class (a) metal ions* are (i) small in size and (ii) are not easily polarised or oxidised. (iii) They have the predominating tendency to combine with non-metal donor atoms possessing similar characteristics. That is, the class (a) acceptors combine well with donor atoms which are small in size and are not easily polarized. Such donor atoms are the first members of VB, VIB and VIIB of the periodic table.

(B) The *class (b) ions* are (i) large in size and (ii) are fairly easily polarizable or oxidizable. (iii) They tend to combine with non-metal donor atoms that are large in size and are easily polarized. S
donor atoms are the heavier members of the periodic Grs.
VIIB.

All the above observations have been elabo
in a generalised manner by Ralph G. Pearson in
*of Soft and Hard Acids and Bases* or the *SHAB co*
of his SHAB concept, Pearson coined the term "*ha*
acceptors and the corresponding donors. He u
for the class (b) acceptors and the corre
SHAB concept a "*soft base*" is one in which
electronegativity, can be easily polarized or
soft donors are associated with the presenc
orbitals on the donor atom. A "*hard base*"
properties. In a hard base, the donor atom is
cannot be easily polarized or oxidised and co
orbitals.

A "*soft acid*" is defined as one posses
following properties : (i) large size, (ii) lo
and (iii) contains several loosely bound ou
easily excited and even removed. A "*ha*
more of the following characteristics: (i)
oxidation state and (iii) absence (or presence

outer electrons which cannot be easily excited or removed to form higher positive oxidation states.

According to the SHAB concept, the principle which can be used for qualitative prediction of the ease of formation and the stabilities of the acid-base or donor-acceptor compounds is, "**Hard acids prefer to bind (coordinate) to the hard bases and the soft acids prefer to bind to the soft bases.**"*

### Experimental criterion of "*softness* and *hardness* of bases

In order to have a practical appreciation of the comparative softness and hardness of different bases, a logical course of action was (i) to select a typical hard acid and a typical soft acid of comparable structural characteristics and (ii) to study the equilibria of the interac-
ions of both of them with different types of bases. Such considerations
to the selection of proton, $H^+$ as *the typical hard acid* and the
thyl mercury (II) cation, $CH_3$-$Hg^+$ as *the typical soft acid.* The
oton satisfies all the characteristics of a hard acid and the methyl
ercury (II) cation have the correct signature of a soft acid. In
tion have

$[CH_3\text{-}Hg(B_2)]^+$. Classification of acids and bases into three categories, **hard, soft** and **borderline** is given below :

TABLE 5.11

Acids

| Hard | Border line | Soft |
|---|---|---|
| $H^+$, $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, | $Fe^{+2}$, $Co^{+2}$, $Ni^{+2}$, $Zn^{+2}$, | $Cu^{+1}$, $Ag^{+1}$, $Au^{+1}$, $Tl^{+1}$, |
| $Be^{+2}$, $Mg^{+2}$, $Ca^{+2}$, $Sr^{+2}$, | $Pb^{+2}$, $Sn^{+2}$, $Sb^{+3}$, $Bi^{+3}$, | $Hg^+$, $Pd^{+2}$, $Cd^{+2}$, $Pt^{+2}$, |
| $Mn^{+2}$, $Al^{+3}$, $Ga^{+3}$, $In^{+3}$, $Se^{+3}$, | $Rh^{+3}$, $Ir^{+3}$, $Ru^{+2}$, $Os^{+2}$, | $Hg^{+2}$, $CH_3Hg^+$, $Pt^{+4}$, |
| $La^{+3}$, $Nd^{+3}$, $Gd^{+3}$, $Lu^{+3}$, | $NO^+$, $SO_2$, $B(CH_3)_3$, | $Te^{+4}$, $Tl^{+3}$, $RS^+$, $I^+$, |
| $Cr^{+3}$, $Co^{+3}$, $Fe^{+3}$, $As^{+3}$, $Si^{+4}$, | $R_3C^+$, $C_6H_5^+$ | $Br^+$, $HO^+$, $RO^+$, $M^\circ$ |
| $Ti^{+4}$, $Zr^{+4}$, $Th^{+4}$, $UO_2^{+2}$, | | (metal atoms) |
| $VO^{+2}$, $(CH_3)_2Sn^{+2}$, $MoO^{+3}$ | | |

Bases

| Hard | Border line | Soft |
|---|---|---|
| $H_2O$, $OH^-$, $F^-$, | $C_6H_5NH_2$, $C_5H_5N$, $N_3^-$, | $R_2S$, $RSH$, $RS^-$, |
| $CH_3COO^-$, $PO_4^{3-}$, $SO_4^{2-}$, | $Br^-$, $NO_2^-$, $S_3^{2-}$ | $I^-$, $SCN^-$, $S_2O_3^{2-}$, |
| $Cl^-$, $CO_3^{2-}$, $ClO_4^-$, $NO_3^-$, | | $R_3P$, $R_3As$, $(RO)_3P$ |
| $ROH$, $RO^-$, $R_2O$, | | $CN^-$, $RNC$, $CO$, |
| $NH_3$, $RNH_2$, $N_2H_4$ | | $C_2H_4$, $C_6H_6$, $H^-$, $R^-$ |

However, it should always be kept in mind that the adjectives "hard" and "soft" are used in a relative sense and it is not possible to divide the acids and bases into two distinctly separate groups. This is the reason why another class (the borderline acids and bases) has to be interposed between the hard and soft categories. Also, in any one group of hard acids (or bases) present in a single row of the previous table, all are not equally hard. Thus, in the group of hard acids represented by the alkali metal ions, the smallest $Li^+$ is the hardest and $Cs^+$, the largest one, is the softest of them. For the same reasons $Mg^{+2}$ is the hardest and $Ba^{+2}$ is the softest acid of the group $Mg^{+2}$, $Ca^{+2}$, $Sr^{+2}$ and $Ba^{+2}$. This line of argument is also applicable to the bases and among the group of bases represented by the halide ions ($F^-$, $Cl^-$, $Br^-$ and $I^-$), the smallest, the most electronegative and the least polarizable $F^-$ ion is the hardest, while the largest, least electronegative and most easily polarizable iodide ion ($I^-$) is the softest base.

**Factors deciding the course of hard-hard and soft-soft interactions**

Why are the hard-hard and soft-soft interactions are preferred to the hard-soft interaction? A complete answer to this question is yet to come out. The reason behind this lack of success appears to be the simultaneous involvement of quite a number of factors whose magnitude is found to vary widely in various types of donor-acceptor interactions. However, the major factors favouring either hard-hard or soft-soft interaction can be singled out.

*Role of electrostatic energy* : As most of the typical hard acids ($H^+$, $Li^+$, $Na^+$, $K^+$ etc.) and the typical hard bases ($F^-$, $OH^-$ etc.) form ionic bonds, **the electrostatic factor** appears to be of greatest importance in hard-hard interactions. Again, it is well known that the **energy of electrostatic interaction* of an ion-pair varies inversely with the distance between the centres of the two interacting ions (inter-ionic distance). Hence, smaller sizes of the interacting acids and bases lead to stronger attraction between them and promote hard-hard interaction.

*Role of covalent factor* : The soft acids and bases being of comparatively larger size and smaller charge in comparison to their harder counterparts, the energy of electrostatic interaction between a soft acid and a soft base is of much smaller magnitude in comparison to that of a hard-hard interaction. Hence, electrostatic factor cannot induce soft-soft interaction. This consideration, along with the easily polarizable character of the soft bases, indicates that **the covalent factor** is of prime importance in causing soft-soft interactions. Higher stability of silver chloride ($Ag^+$ being a soft acceptor) in comparison to that of silver fluoride ($F^-$ being a hard base) is a clear indication of the dominating role of the covalent factor, because in AgCl, the $Ag-Cl$ bond has much greater covalent character than the $Ag-F$ bond. Extreme instability of silver hydroxide (AgOH, being a combination of soft acid and hard base) also supports the above conclusion.

*Role of π-bonding* : Many of the soft metal ions have (i) low oxidation state and (ii) quite a number of '*d*' electrons, and both of these factors favour metal to ligand π-bonding. Again, many of the soft bases like, CO, $PR_3$, $P(OR)_3$, $AsR_3$, $I^-$ etc. are π-bonding ligands. Hence, π-bonding definitely plays a very important role in promoting soft-soft interactions.

**Applications of the SHAB concept**

The SHAB concept has been successfully applied to a variety of chemical problems. But, here we will point out only a few of the more familiar cases.

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*Electrostatic energy is often referred to as Madelung energy.

(i) *Explanation of the relative stabilities of different types of acid-base combination :* It is well known that $[AgI_2]^-$ is stable but the stability of the $[AgF_2]^-$ species is so small that it does not exist in the solid state. This is because $Ag^+$, being a soft acid, can form a stable complex with the soft-base $I^-$, but cannot form a stable species with the very hard base $F^-$. Explanation of the greater stability of AgCl over AgF and the non-existence of AgOH has already been cited.

(ii) *Occurrence of the ores of certain metals* : Hard acids such as $Mg^{+2}$, $Ca^{+2}$, $Al^{+3}$ are found to occur in nature as their carbonates and oxides (e.g. $MgCO_3$, $CaCO_3$, $Al_2O_3$), $CO_3^{2-}$ and $O^{2-}$ being hard bases. They do not occur as sulphides (e.g. MgS, CaS, $Al_2S_3$) because $S^{2-}$ is a soft acid. On the otherhand, soft acids like $Ag^{+1}$ and $Hg^{+2}$ occurs mainly as sulphides and not as oxides.

(iii) *Choice of catalysts for particular reactions* : Metals are soft acids and therefore adosrb soft bases effectively and so metal catalysts should be used where the reactions is of soft-soft type.

(iv) *Predicting solubility of different solutes in different types of solvents* : Hard solutes go into solution in hard solvents and the soft solvents tend to dissolve soft solutes. Thus, NaF (a hard solute made up of the hard acid $Na^+$ and the hard base $F^-$) is soluble in the hard solvent water ($H_2O$ being considered as a combination of the hard acid $H^+$ and hard base $OH^-$), but is not soluble in softer solvents like alcohols. Again, soft solute ethyl acetate dissolves in soft solvents like alcohol or benzene, but does not dissolve in a hard solvent like water.

The SHAB concept has also been applied for the successful prediction of relative speeds of both electrophilic and nucleophilic substitution reactions and it is now clear that the SHAB concept is applicable to many aspects of chemical reactions. However, the strictly qualitative nature of the concept imposes a severe limitation on its application to the problem of interpretation of intrinsic strengths of acids and bases.

CHAPTER VI

# OXIDATION AND REDUCTION PROCESSES

The vast number of reactions encountered in the domain of chemistry can be broadly classified into several *types* or *classes*. Such classification of chemical reactions is very helpful in the sense that, it reduces the almost super-human task of learning about each and every one of the huge number of apparently diverse chemical reactions, to the study of a few general types, — each type or class being characterised by some common characteristics. We are familiar with the reactions like that of hydrogen and chlorine which forms hydrochloric acid : $H_2+Cl_2 = 2HCl$. Such a reaction is called a *direct union* or *combination* reaction. Similarly, the splitting up of hydrogen peroxide into water and oxygen, $2H_2O_2 = 2H_2O+O_2$, is termed a *decomposition* reaction.

The reaction, $NH_3+HCl = NH_4Cl$, is an *acid-base reaction* or *neutralisation.* Conversion of methane to methyl chloride (or to $CH_2Cl_2$, $CHCl_3$ and $CCl_4$), *viz.* $CH_4+Cl_2 = CH_3Cl+HCl$, is called a *substitution* reaction, and the conversion of ethylene into ethane (in presence of nickel catalyst) by its reaction with hydrogen, $C_2H_4+H_2 = C_2H_6$, is known as an *addition reaction.* Several other classes of chemical reactions are also recognised, among which *oxidation-reduction reactions* are of immense importance. These reactions form the subject-matter of our disscussion in this chapter. Originally, the term *oxidation* was used to denote chemical reactions in which substances *acquired oxygen,* while the term *reduction* was used to designate the reverse process, *viz.* the *removal of oxygen* from or addition of hydrogen to a compound. But, our present knowledge about oxidation-reduction or the *redox* phenomenon, has undergone a radical change as a result of our understanding of the electronic structure of the atoms and the mechanism of the process through which chemical bonding takes place.

## OXIDATION AND REDUCTION DEFINED.

A process in which electrons are lost is termed as *oxidation,* and *reduction* is a process in which electrons are taken up or gained. Thus, we can say that, *loss of electron(s) means oxidation* and *gain in electron(s) is reduction.* Let us consider the reaction between sodium and chlorine to form sodium chloride. This reaction takes place spontaneously when the two reactants are brought in contact with each other : $Na+\frac{1}{2}Cl_2 = Na^+Cl^-$ .. .. (6.1)

This reaction can be broken up into two *half-reactions,*

$$Na \longrightarrow Na^+ + e \text{ (oxidation)}$$
$$\text{and } \tfrac{1}{2}Cl_2+e \longrightarrow Cl^- \text{ (reduction).}$$

In the first *half-reaction*, one electron is *lost* by the sodium atom, leading to the formation of the $Na^+$ ion, and hence we can say that the sodium atom has undergone *oxidation* to the $Na^+$ ion *by the loss of one electron.*

In the second *half-reaction*, one electron is *gained* by the chlorine atom, forming the chloride ion. Thus, it is an example of *reduction* where the chlorine atom is reduced to a chloride ion.

Here, the electron lost by the sodium atom is gained by the chlorine atom and by this process of *mutual loss and gain of an electron*, the $Na^+$ and the $Cl^-$ ions are formed. This clearly illustrates the complementary character of the oxidation-reduction process. This is true for *all* oxidation-reduction reactions. Whenever there is a process of oxidation or electron-loss, a process by which the lost electrons are taken up (*i.e.* reduction) must also take place. Oxidation and reduction processes can only occur *simultaneously*, and never alone.

## OXIDISING AND REDUCING AGENTS.

In the reaction between the sodium atom and the chlorine atom, the sodium atom loses one electron, is oxidised into the $Na^+$ ion, and is known as the *reducing agent* or *reductant*. The electron lost by the sodium atom is taken up by the chlorine atom, which is *reduced* to the chloride ion, and is called an *oxidising agent* or *oxidant*. Thus, we can say that, *a reducing agent or a reductant is a substance which supplies electron(s) and reduces other substances, itself being oxidised in the process.* Similarly, *oxidising agents are substances which take up electron(s) supplied by the reductant and themselves undergo reduction.* Thus, the chlorine atom is the oxidising agent in reaction 6·1, since it *gains* the electron that is lost by the reducing agent sodium atom and is thereby reduced to the chloride ion.

We will now consider another familiar reaction, *viz.* the liberation of hydrogen gas from HCl by metallic zinc :

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow.$$

Here, in $ZnCl_2$, zinc is present as $Zn^{++}$. The zinc atom has lost 2 electrons and is oxidised to $Zn^{++}$. Hence, Zn is the reducing agent here. Similarly, the $H^+$ in HCl has taken up electron supplied by the zinc atom, and is reduced into neutral hydrogen atom. Hence it is the oxidising agent. This reaction can be broken up into two half-reactions of reduction and oxidation as :

$$\begin{array}{llcll}
2\mathrm{H}^{+} & +2e & = & \mathrm{H}_2 & \text{(reduction)}\\
\text{Oxidant}_1 & & & \text{Reductant}_1 & \\
\mathrm{Zn} & & = & \mathrm{Zn}^{++} + 2e & \text{(oxidation)}\\
\text{Reductant}_2 & & & \text{Oxidant}_2 & \\
\hline
2\mathrm{H}^{+} & +\mathrm{Zn} & = & \mathrm{H}_2\uparrow \quad +\mathrm{Zn}^{++} & \quad .. \quad (6.2)\\
\mathrm{Ox}_1 & \mathrm{Red}_2 & & \mathrm{Red}_1 \quad \mathrm{Ox}_2 &
\end{array}$$

In a general way, the reaction 6·2 and all other red-ox reactions may be written as :

$$\begin{array}{lcll}
a\ \mathrm{Ox}_1+ne & = & a\ \mathrm{Red}_1 & \text{(reduction)}\\
b\ \mathrm{Red}_2 & = & b\ \mathrm{Ox}_2 + ne & \text{(oxidation)}\\
\hline
a\ \mathrm{Ox}_1+b\ \mathrm{Red}_2 & = & a\ \mathrm{Red}_1+b\ \mathrm{Ox}_2 &
\end{array}$$

Thus we find that, in a redox reaction the electrons are generated in the oxidation-half and are transferred to the reduction-half where they are accepted.

Half-reactions involving the loss or gain of electrons are also called *electrode reactions* or *electron reactions.* These reactions take place at the electrodes. Thus, *oxidation occurs at the anode* or the positive electrode which can accept the electrons released due to oxidation. *Reduction occurs at the negative electrode* or *cathode* which supplies electrons. Such reactions also take place by the direct contact of atoms, ions or molecules, the contact causing exchange of electrons between the oxidant and the reductant.

## BALANCING OF RED-OX REACTIONS BY THE ION-ELECTRON METHOD.

Reactions involving oxidation and reduction are not always so simple as the ones cited above. A large number of red-ox reactions involve several reactants in various molar ratios, involving a changeover of quite a number of electrons. The balancing of such red-ox reactions often poses quite a problem to the students. But, remembering that most of the common redox reactions take place in *aqueous medium* and are of *ionic nature*, some empirical rules can be framed, which help one to balance even the more complicated red-ox reactions. These rules are :

(1) All the reactants and products are ascertained and the complete reaction is split up into two half-reactions, one for oxidation and the other for reduction.

(2) Each half-reaction is balanced not only with respect to the *number of atoms of each kind*, but also with respect of the *positive and negative charges*. When the reaction is taking place in aqueous medium, $H_2O$ or ions $H^+$ and $OH^-$ may be added, keeping in mind *that in no reaction both* $H^+$ *and* $OH^-$ *ions should occur together*.

(3) In acidic solution, $H^+$ ions and $H_2O$ molecules may be added to any half-reaction, while in an alkaline solution, $OH^-$ ions and $H_2O$ molecules may be added.

(4) $H_2O$ molecules are to be added to the side deficient in oxygen and $H^+$ ions are to be added to the side deficient in hydrogen.

(5) When the electrons on the two half-reactions are not equal, one or both half-reactions should be multiplied by the smallest suitable integer, so that the electrons in both the half-reactions become equal.

(6) The two balanced half-reactions are then added up, cancelling the common terms whenever present.

We will now proceed to illustrate the above procedure with the help of some redox reactions.

Ferrous ion is oxidised by dichromate in acid solution to the ferric state, the latter being reduced to chromic salts. In this reaction, the $Cr_2O_7^{2-}$ ion is the oxidant and the $Fe^{+2}$ ion is the reductant. Since the reaction occurs in acid solution, the left-hand side of the overall reaction will contain the reactants $Cr_2O_7^{2-}$, $Fe^{+2}$ and $H^+$, while the right-hand side will contain the products $Cr^{+3}$, $Fe^{+3}$ and $H_2O$. Thus, we have ascertained all the reactants and products of the reaction.

The partial ionic equation for the reduction of the oxidant, $Cr_2O_7^{2-}$, will be $Cr_2O_7^{2-} \longrightarrow 2Cr^{+3}$.

Since it takes place in acid solution, $H^+$ ions will take part and since the fate of oxygen present in the oxidant is its conversion into $H_2O$ molecules, we will use $14H^+$ to convert seven oxygen atoms of $Cr_2O_7^{2-}$ to 7 $H_2O$. Thus, we may write,

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{+3} + 7H_2O.$$

The number of atoms are now balanced on both sides, but the charges are not. The resultant charge on the left side is $(+14-2) = +12$, while that in the right side is $+6$. Thus, to balance the charges on both sides, we add six electrons to the left side :

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{+3} + 7H_2O. \quad .. \quad (a)$$

Similarly, for the oxidation of the reductant, $Fe^{+2}$, we write :

$$Fe^{+2} \longrightarrow Fe^{+3},$$

and for balancing charges on both sides, we can write,

$$Fe^{+2} \longrightarrow Fe^{+3} + e.$$

The electrons involved in the reduction of the oxidant is 6, while that in the oxidation of the reductant is 1. So, to balance the number of electrons in both the half-reactions, we multiply the last eqn. by 6 :

$$6Fe^{+2} = 6Fe^{+3} + 6e \quad \ldots \quad \ldots \quad (b)$$

Now we add up (a) and (b),

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e & \longrightarrow & 2Cr^{+3} + 7H_2O \\ 6Fe^{+2} & \longrightarrow & 6Fe^{+3} + 6e \\ \hline Cr_2O_7^{2-} + 6Fe^{+2} + 14H^+ & = & 2Cr^{+3} + 6Fe^{+3} + 7H_2O \end{array}$$

This is the final form of the ionic redox reaction between $Cr_2O_7^{2-}$ and $Fe^{+2}$ in acid medium, perfectly balanced from the point of view of the number of atoms as well as of charges.

A few more illustrations of balancing red-ox reactions by *ion-electron method* are now given. Dichromate reacts with acidified potassium iodide solution, producing iodine, itself being reduced to $Cr^{+3}$.

$$\begin{array}{rcl} 6 \times (I^- & \rightarrow & \frac{1}{2}I_2 + e) \\ Cr_2O_7^{2-} + 14H^+ + 6e & \rightarrow & 2Cr^{+3} + 7H_2O \\ \hline 6I^- + Cr_2O_7^{2-} + 14H^+ & = & 2Cr^{+3} + 3I_2 + 7H_2O \end{array}$$

Acidified (HCl) dichromate reacts with sulphite, producing sulphate and chromic chromium.

$$\begin{array}{rcl} 3 \times (SO_3^{2-} + H_2O & \rightarrow & SO_4^{2-} + 2H^+ + 2e) \\ Cr_2O_7^{2-} + 14H^+ + 6e & \rightarrow & 2Cr^{+3} + 7H_2O \\ \hline 3SO_3^{2-} + Cr_2O_7^{2-} + 8H^+ & = & 3SO_4^{2-} + 2Cr^{+3} + 4H_2O \end{array}$$

Hydrogen sulphide ($H_2S$) reduces acidified ($H_2SO_4$) dichromate solution from orange to green, forming chromic sulphate and precipitating sulphur.

$$\begin{array}{rcl} 3 \times (H_2S & \rightarrow & 2H^+ + S + 2e) \\ Cr_2O_7^{2-} + 14H^+ + 6e & \rightarrow & 2Cr^{+3} + 7H_2O \\ \hline 3H_2S + Cr_2O_7^{2-} + 8H^+ & = & 2Cr^{+3} + 3S + 7H_2O \end{array}$$

In alkaline solution, permanganate oxidises sodium stannite ($Na_2SnO_2$) to sodium stannate ($Na_2SnO_3$) and is itself reduced to manganese dioxide, $MnO_2$.

$$\begin{array}{rcl} 2 \times (MnO_4^- + 2H_2O + 3e & \rightarrow & MnO_2 + 4OH^-) \\ 3 \times (SnO_2^{2-} + 2OH^- & \rightarrow & SnO_3^{2-} + H_2O + 2e) \\ \hline 2MnO_4^- + 3SnO_2^{2-} + H_2O & = & 2MnO_2 + 3SnO_3^{2-} + 2OH^- \end{array}$$

In neutral solution, permanganate oxidises manganous ion to $MnO_2$, while $MnO_4^-$ itself is reduced to $MnO_2$.

$$\begin{array}{ll} 2 \times (MnO_4^- + 2H_2O + 3e & \rightarrow MnO_2 + 4OH^-) \\ 3 \times (Mn^{+2} + 4OH^- & \rightarrow MnO_2 + 2H_2O + 2e) \\ \hline 2MnO_4^- + 3Mn^{+2} + 4OH^- & = 5MnO_2 + 2H_2O \end{array}$$

[This is the principle of Volhard's method of rapid volumetric determination of manganese. The reaction is carried out in water medium in presence of a suspension of the amphoteric oxide, ZnO, which neutralises both $H^+$ and $OH^-$, if any one is generated in excess.]

In a slightly acid or neutral solution, iodine reacts with sodium thiosulphate ($Na_2S_2O_3$), producing sodium tetrathionate ($Na_2S_4O_6$), and itself is reduced to iodide.

$$\begin{array}{ll} 2 \times (\tfrac{1}{2}I_2{}^\circ + e & \rightarrow I^-) \\ 2\,S_2O_3{}^{2-} & \rightarrow S_4O_6{}^{2-} + 2e^- \\ \hline I_2{}^\circ + 2S_2O_3{}^{2-} & = S_4O_6{}^{2-} + 2I^- \end{array}$$

In hydrochloric acid solution, stannous chloride reduces mercuric mercury ($Hg^{+2}$) to the mercurous ($Hg^{+1}$) state, itself being oxidised to $Sn^{+4}$.

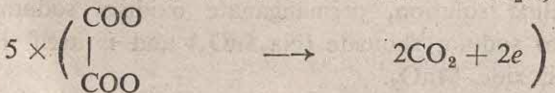
$$\begin{array}{ll} 2 \times (Hg^{+2} + e & \rightarrow Hg^{+1}) \\ Sn^{+2} & \rightarrow Sn^{+4} + 2e \\ \hline 2Hg^{+2} + Sn^{+2} & = Sn^{+4} + 2Hg^{+1}. \end{array}$$

Cupric copper ($Cu^{+2}$) oxidises iodide in slightly acid solution and liberates iodine, while it is reduced to $Cu^{+1}$ which is pptd as $Cu_2I_2$

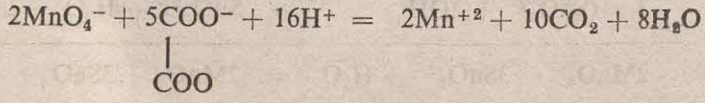
$$\begin{array}{ll} 2Cu^{+2} + 2e & \rightarrow 2Cu^{+1} \\ 2I^- & \rightarrow I_2{}^\circ + 2e \\ \hline 2Cu^{+2} + 2I^- & = 2Cu^{+1} + I_2{}^\circ \end{array}$$

Permanganate oxidises oxalic acid or oxalate in acid solution to carbon dioxide and itself is reduced to the manganous state.

$$2 \times (MnO_4^- + 8H^+ + 5e \rightarrow Mn^{+2} + 4H_2O)$$



$$5 \times \left( \begin{array}{c} COO \\ | \\ COO \end{array} \longrightarrow 2CO_2 + 2e \right)$$



$$2MnO_4^- + 5\begin{array}{c} COO^- \\ | \\ COO \end{array} + 16H^+ = 2Mn^{+2} + 10CO_2 + 8H_2O$$

In acid medium, stannous compounds reduce ferric iron to the ferrous state. The stannous tin is oxidised to the stannic state.

$$\begin{array}{lll} 2 \times (Fe^{+3} + e & \rightarrow & Fe^{+2}) \\ Sn^{+2} & \rightarrow & Sn^{+4} + 2e \\ \hline 2Fe^{+3} + Sn^{+2} & = & 2Fe^{+2} + Sn^{+4} \end{array}$$

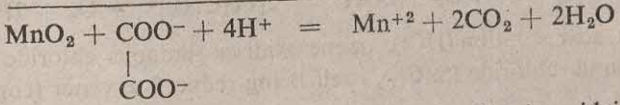
Permanganate oxidises hydrogen peroxide to oxygen and itself is reduced to the manganous state, the reaction taking place in sulphuric acid medium.

$$\begin{array}{lll} 2 \times (MnO_4^- + 8H^+ + 5e & \rightarrow & Mn^{+2} + 4H_2O) \\ 5 \times (H_2O_2 & \rightarrow & 2H^+ + O_2 + 2e) \\ \hline 2MnO_4^- + 5H_2O_2 + 6H^+ & = & 2Mn^{+2} + 8H_2O + 5O_2 \uparrow \end{array}$$

In dilute sulphuric acid solution, manganese dioxide oxidises oxalic acid to carbon dioxide, producing manganous species.

$$MnO_2 + 4H^+ + 2e \rightarrow Mn^{+2} + 2H_2O$$

$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array} \rightarrow 2CO_2 + 2e$$



$$MnO_2 + \begin{array}{l} COO^- \\ | \\ COO^- \end{array} + 4H^+ = Mn^{+2} + 2CO_2 + 2H_2O$$

Manganese dioxide oxidises concentrated hydrochlonic acid into elemental chlorine on heating, itself being reduced to the maganous state.

$$\begin{array}{lll} MnO_2 + 4H^+ + 2e & \rightarrow & Mn^{+2} + 2H_2O \\ 2 \times [Cl^- & \rightarrow & \frac{1}{2}Cl_2^{\circ} + e] \\ \hline MnO_2 + 4H^+ + 2Cl^- & = & Mn^{+2} + Cl_2 \uparrow + 2H_2O \end{array}$$

In dilute $H_2SO_4$ medium, $MnO_2$ (freshly pptd.) oxidises ferrous iron to the ferric state and $MnO_2$ is reduced to the manganous state.

$$\begin{array}{lll} MnO_2 + 4H^+ + 2e & \rightarrow & Mn^{+2} + 2H_2O \\ 2 \times [Fe^{+2} & \rightarrow & Fe^{+3} + e] \\ \hline MnO_2 + 2Fe^{+2} + 4H^+ & = & Mn^{+2} + Fe^{+3} + 2H_2O \end{array}$$

In nitric acid solution, lead dioxide ($PbO_2$) or red lead ($Pb_3O_4$) oxidises manganous ion ($Mn^{+2}$) to permanganate ($MnO_4^-$) and $PbO_2$ is reduced to $Pb^{+2}$.

$$\begin{array}{lll} 5 \times [PbO_2 + 4H^+ + 2e & \rightarrow & Pb^{+2} + 2H_2O] \\ 2 \times [Mn^{+2} + 4H_2O & \rightarrow & MnO_4^- + 8H^+ + 5e] \\ \hline 5PbO_2 + 2Mn^{+2} + 4H^+ & = & 2MnO_4^- + 5Pb^{+2} + 2H_2O \end{array}$$

In acid solution, permanganate oxidises iodide to iodine, itself being reduced to manganous ion.

$$\begin{array}{ll}
2 \times [\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5e & \rightarrow \mathrm{Mn^{+2}} + 4\mathrm{H_2O}] \\
10 \times [\mathrm{I^-} & \rightarrow \tfrac{1}{2}\mathrm{I^\circ} + e] \\
\hline
2\mathrm{MnO_4^-} + 10\mathrm{I^-} + 16\mathrm{H^+} & = 2\mathrm{Mn^{+2}} + 5\mathrm{I_2} + 8\mathrm{H_2O}
\end{array}$$

On being heated with NaOH (or KOH) solution, zinc dust reduces $\mathrm{OH^-}$ to hydrogen, itself being oxidised to the zincate ion ($\mathrm{ZnO_2^{-2}}$).

$$\begin{array}{l}
2\mathrm{H_2O} + 2e \rightarrow 2\mathrm{OH^-} + \mathrm{H_2} \\
\mathrm{Zn} + 4\mathrm{OH^-} \rightarrow \mathrm{ZnO_2^-} + 2\mathrm{H_2O} + 2e \\
\hline
\mathrm{Zn} + 2\mathrm{OH^-} = \mathrm{ZnO_2^-} + \mathrm{H_2}\uparrow
\end{array}$$

In alkaline solution (NaOH or KOH), hydrogen peroxide ($\mathrm{H_2O_2}$) reduces potassium ferricyanide $\mathrm{K_3[Fe(CN)_6]}$, to potassium ferrocyanide $\mathrm{K_4[Fe(CN)_6]}$, itself being oxidised to oxygen ($\mathrm{O_2}$).

$$\begin{array}{ll}
2 \times (\,[\mathrm{Fe(CN)_6}]^{3-} + e & \rightarrow [\mathrm{Fe(CN)_6}]^{4-}) \\
\mathrm{H_2O_2} + 2\mathrm{OH^-} & \rightarrow 2\mathrm{H_2O} + \mathrm{O_2} + 2e \\
\hline
2[\mathrm{Fe(CN)_6}]^{3-} + \mathrm{H_2O_2} + 2\mathrm{OH^-} & = 2[\mathrm{Fe(CN)_6}]^{4-} + \mathrm{O_2} + 2\mathrm{H_2O}
\end{array}$$

In acid solution (HCl), ozone oxidises stannous chloride ($\mathrm{SnCl_2}$) into stannic chloride ($\mathrm{SnCl_4}$), itself being reduced to water (containing $\mathrm{O^{2-}}$ ion).

$$\begin{array}{ll}
\mathrm{O_3} + 6\mathrm{H^+} + 6e & \rightarrow 3\mathrm{H_2O} \\
3 \times [\mathrm{Sn^{+2}} & \rightarrow \mathrm{Sn^{+4}} + 2e] \\
\hline
\mathrm{O_3} + 3\mathrm{Sn^{+2}} + 6\mathrm{H^+} & = 3\mathrm{Sn^{+4}} + 3\mathrm{H_2O}
\end{array}$$

Hot and concentrated $\mathrm{HNO_3}$ oxidises metallic copper to cupric nitrate, itself being reduced to nitrogen dioxide.

$$\begin{array}{ll}
2 \times [\mathrm{NO_3^-} + 2\mathrm{H^+} + e & \rightarrow \mathrm{NO_2} + \mathrm{H_2O}] \\
\mathrm{Cu^\circ} & \rightarrow \mathrm{Cu^{+2}} + 2e \\
\hline
2\mathrm{NO_3^-} + \mathrm{Cu^\circ} + 4\mathrm{H^+} & = \mathrm{Cu^{+2}} + 2\mathrm{NO_2} + 2\mathrm{H_2O}
\end{array}$$

In acidic solution, bromine (or $\mathrm{Cl_2}$ or $\mathrm{I_2}$) oxidises sulphite into sulphate, itself being reduced to bromide ion.

$$\begin{array}{lll}
\mathrm{Br_2} + 2e & \longrightarrow & 2\mathrm{Br^-} \\
\mathrm{SO_3^{2-}} + \mathrm{H_2O} & \longrightarrow & \mathrm{SO_4^{2-}} + 2\mathrm{H^+} + 2e \\
\hline
\multicolumn{3}{l}{\mathrm{Br_2} + \mathrm{SO_3^{2-}} + \mathrm{H_2O} = \mathrm{SO_4^{2-}} + 2\mathrm{Br^-} + 2\mathrm{H^+}}
\end{array}$$

## EQUIVALENT WEIGHTS OF OXIDISING AND REDUCING AGENTS.

The equivalent weight of an oxidising agent or a reducing agent is the weight, which takes up or gives up one mole of electrons. In a different way, the equivalent weight of an oxidant or a reductant is its formula weight divided by the number of electrons taken up by the oxidant or given up by the reductant in a given reaction. The best way of calculating the equivalent weights of oxidants or reductants is to set up the partial ionic equations for the oxidant or the reductant and ascertain the number of electrons involved per formula weight of the reagent. To illustrate this statement, we consider the oxidation of ferrous ion to ferric ion by potassium permanganate in acid medium. The partial ionic eqn. for the oxidant is

$$MnO_4^- \text{ is, } MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{+2} + 4H_2O.$$

Hence, we find that the number of electrons involved per mole of permanganate is 5. Thus, the equivalent weight of $KMnO_4$, here, is

$$\frac{\text{Formula wt. of } KMnO_4}{5} = \frac{39{\cdot}1+54{\cdot}94+64}{5} = \frac{158{\cdot}04}{5} = 31{\cdot}608.$$

Thus, we can say that, 31·608 gms. of $KMnO_4$ gain one mole of electrons. when it oxidises $Fe^{+2}$ to $Fe^{+3}$ in acid solution.

To prepare a 1 (N) solution of $KMnO_4$, one has to weigh out 31·608 gms. of $KMnO_4$, dissolve it in distilled water and make the final volume of the solution one litre. One litre of a 0·1 (N) $KMnO_4$ solution may be prepared in the same manner using 3·1608 gms. of $KMnO_4$.

**The equivalent weights of oxidants and reductants are not absolute constants.**

The equivalent weight of an oxidant or a reductant depends upon the actual reaction, and is not always identical. We have already seen that the equivalent weight or $KMnO_4$ in acid solution is $\frac{\text{Formula wt.}}{5}$. However, in alkaline or neutral medium, instead of being reduced to $Mn^{+2}$, it forms $MnO_2$, containing $Mn^{+4}$ :

$$MnO_4^- + 4H^+ + 3e \longrightarrow MnO_2 \downarrow + 2H_2O.$$

$$\text{So, here, the equivalent wt. of } KMnO_4 = \frac{\text{Formula wt.}}{3}.$$

Again, in presence of excess fluoride ions, $MnO_4^-$ is reduced to $[MnF_6]^{3-}$, containing $Mn^{+3}$ :

$$MnO_4^- + 8H^+ + 6F^- + 4e \longrightarrow [MnF_6]^{3-} + 4H_2O.$$

The equivalent wt. of $KMnO_4$, here, is $\frac{\text{Formula wt.}}{4}$.

Hence, while mentioning the equivalent weights of oxidants or reductants, the *exact reaction-conditions*, along with *the particular reaction in which it takes part*, must be mentioned.

Let us now consider the partial ionic eqn. of the reductant, ferrous sulphate : $Fe^{+2} \rightarrow Fe^{+3} + e$

The equivalent weight of ferrous sulphate is $\frac{\text{Formula wt.}}{1}$, *i.e.*, its formula weight.

When only one electron is taken up or given out by an oxidant or a reductant, its equivalent weight and formula weight are the same. The following table contains some useful informations about the more important and commonly used oxidising and reducing agents.

TABLE 6.1

| Oxidising/Reducing agent | | Partial ionic equation | Equivalent wt. $=\frac{\text{Formula wt.}}{\text{number of electrons involved}}$ |
|---|---|---|---|
| Mol. formula | Formula wt. | | |
| $KMnO_4$ | 158.04 | $MnO_4^-+8H^++5e \rightarrow Mn^{+2}+4H_2O$ (in acid medium) | $\frac{\text{Formula wt.}}{5}=\frac{158.04}{5}=31.608$ |
| $K_2Cr_2O_7$ | 294.19 | $Cr_2O_7^{2-}+14H^++6e \rightarrow 2Cr^{+3}+7H_2O$ | $\frac{\text{Formula wt.}}{6}=\frac{294.19}{6}=49.03$ |
| $KIO_3$ | 214.006 | $IO_3^-+6H^++5e \rightarrow \frac{1}{2}I_2^0+3H_2O$ | $\frac{\text{Formula wt.}}{5}=\frac{214.006}{5}=42.80$ |
| $I_2$ | 253.809 | $I^0_2+2e \rightarrow 2I^-$ | $\frac{\text{Formula wt.}}{2}=\frac{253.809}{2}=126.90$ |
| KI | 166.01 | $I^- \rightarrow \frac{1}{2}I_2^0+e$ | $\frac{\text{Formula wt.}}{1}=\frac{166.01}{1}=166.01$ |
| $FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr Salt) | 391.87 | $Fe^{+2} \rightarrow Fe^{+3}+e$ | $\frac{\text{Formula wt.}}{1}=\frac{391.87}{1}=391.87$ |
| $CuSO_4.5H_3O$ | 249.54 | $Cu^{+2}+e \rightarrow Cu^{+1}$ | $\frac{\text{Formula wt.}}{1}=\frac{249.54}{1}=249.54$ |
| $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}.2H_2O$ | 126 | $\begin{array}{l}COO^-\\ \vert\\ COO^-\end{array} \rightarrow 2CO_2+2e$ | $\frac{\text{Formula wt.}}{2}=\frac{126}{2}=63$ |
| $Na_2S_2O_3.5H_2O$ | 248 | $2S_2O_3^{2-} \rightarrow S_4O_6^{2-}+2e$ | $\frac{\text{Formula wt.}}{1}=\frac{248}{1}=248$ |

We have already mentioned that half-reactions, constituting a redox process, frequently occur at the electrodes, *i.e.*, many redox reactions may be visualised as electrochemical reactions taking place inside appropriate electrochemical cells. The study of electrochemical reactions, occuring inside electrochemical cells, helps us to understand the quantitative aspects of oxidation-reduction processes. Hence, before considering the quantitative aspects of the redox phenomenon, we should be well-conversant with the principles and working-mechanism of the electrochemical cells.

Before entering into the actual details of electrochemical cells, we will discuss some preliminary ideas about the conduction of electric current through aqueous solutions, and the substances which cause such conduction of current.

## INSULATORS AND CONDUCTORS.

Materials like glass, porcelain, plastics, bakelite, mica *etc.* resist the flow of electric current through them, and are called *insulators.* Other substances like the metals (Cu, Ag, Al *etc.*), aqueous solutions of acids, bases and salts, and some metal salts in the molten condition, allow a facile passage of electric current through them, and are termed *conductors.* Conductors are of two types, *electronic conductors* and *electrolytic conductors* or *electrolytes.* In the electronic conductors like the metals and their alloys, electricity is carried by the transference of electrons, and there is no transportation of matter through them during the passage of electricity. When put in solution or melted, the electrolytic conductors or electrolytes are dissociated into their component ions before the passage of electricity, and the subsequent flow of current through them is associated with the transport of matter to each of the electrodes. Let us consider an electrolyte (AB) which dissociates as, $AB \rightleftharpoons A^+ + B^-$. On the passage of electric current, the positive ions or cations ($A^+$) move towards the negative electrode or cathode, and the negative ions or anions migrate to the positive electrode or anode, where they get discharged as the respective elements or radicals, as the case may be. The liberated species may undergo further secondary reactions with the medium, in which they are generated, giving rise to newer and different products. The examples cited below will illustrate this point.

$$\underset{\text{electrolyte}}{2HCl} \overset{\text{dissociation}}{\rightleftharpoons} \underset{\text{cation}}{2H^+} + \underset{\text{anion}}{2Cl^-} \xrightarrow[\text{current}]{\text{electric}} \underset{\text{at cathode}}{H_2\uparrow} + \underset{\text{at anode}}{Cl_2\uparrow}$$

$$CuSO_4 + H_2O \overset{\text{dissociation}}{\rightleftharpoons} Cu^{++} + SO_4^{2-} + H_2O \xrightarrow[\text{current}]{\text{electric}} \underset{\text{at cathode}}{Cu^{\circ}}$$

$$+ 2H^+ + SO_4^{2-} + \underset{\text{(oxygen is liberated at anode)}}{\tfrac{1}{2}O_2 \uparrow}$$

We find here that the electrical energy is being converted into chemical energy, causing chemical reactions at anode and cathode, and this is known as the process of *electrolysis.*

It is evident that such electrolytic reactions are not spontaneous and can occur only under the driving influence of the electric current, which supplies electrons to the cathode and removes electrons from the anode.

It is quite logical to assume that, if electrical energy can be used to bring about chemical changes, the energy involved in a chemical reaction can also be converted into electrical energy. But, to bring about such an energy-transformation, an *appropriate* chemical reaction, which takes place *spontaneously*, must be *brought about* under suitable conditions. Such a device, in which the energy of a chemical process is converted into electrical energy, is called an *electro-chemical cell*, a *galvanic cell* or a *voltaic cell.*

Since electric current is a flow of electrons, a chemical reaction leading to the generation of electric current must be one, in which an oxidant and a reductant react spontaneously with each other, (the reductant supplying the electrons and the oxidant accepting them), both of them being connected by an electronic conductor, allowing a facile passage of the electrons. However, the arrangement must be made in a way so that the oxidant and the reductant must not be allowed to come in direct contact with each other. If it so happens, no electrical energy can be extracted from the system.

Electrochemical cells are widely used in our daily life. Daniel cell, Lechlance cell and different storage cells are used in the laboratory. The acid storage cells are used in automobiles and in the laboratory. Dry torch cells and dry batteries are used widely as source of electrical energy, when small and steady current for short periods is required. To illustrate a typical electrochemical cell, we will discuss the affairs of the familiar *Daniel cell.* It consists of a glass vessel separated into two compartments by means of a porous porcelain plate. In one compartment, a zinc rod is dipped into a zinc sulphate solution and in the other, a copper rod is kept immersed in a copper sulphate solution

(Fig. 6.1). The porous barrier allows the diffusion of positive and negative ions in opposite directions through itself, but prevents direct mixing of the two solutions. Zinc and copper rods are the two electrodes. When the two electrodes are connected externally by a metal (Cu, Al) wire through an ammeter, the ammeter indicates that electrons are flowing from the zinc rod to the copper rod. If current is drawn from the cell, the zinc rod starts dissolving and the copper rod grows in weight due to the deposition of copper. This is a direct evidence that the electricity generated is due to a chemical reaction. In order to understand the mechanism of the process occuring inside the cell, we note that the electrons flow from the zinc rod through the external circuit towards the copper rod, and zinc dissolves from the rod as $Zn^{+2}$ ions : $Zn \rightleftharpoons Zn^{+2}(aq.) + 2e$ .. (a)

(oxidation or electron-loss at the zinc rod)

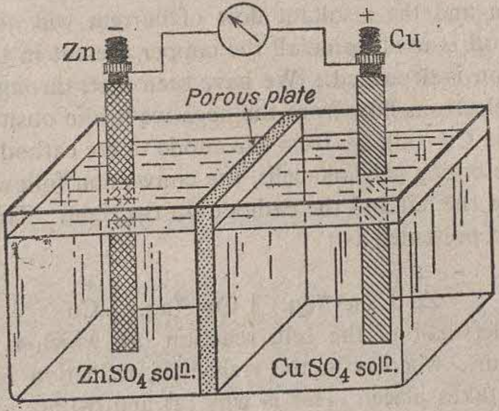


Fig. 6.1

It is also observed that, as the electrons flow to the copper rod, $Cu^{+2}$ ions leave the solution and get deposited on the copper rod as metallic copper : $Cu^{+2}(aq.) + 2e \longrightarrow Cu(s)$ .. (b)

(reduction or electron-gain at the copper rod)

The overall reaction is :

$Zn(s) + Cu^{+2}(aq.) \rightarrow Cu(s) + Zn^{+2}(aq.)$ .. (c)

This overall reaction tells us what goes on in the entire electrochemical cell. Thus, when zinc atoms from the zinc rod dissolve, producing $Zn^{+2}$ ions, they leave behind two electrons for each $Zn^{+2}$ ion produced and make the zinc rod electron-rich and hence *negatively charged.* Similarly, since $Cu^{+2}$ ions get discharged on the copper rod by taking up two electrons for each $Cu^{+2}$ ion discharged, the copper electrode becomes electron-deficient and hence *positively charged.* Thus, the copper rod is the positive electrode of the cell. In other words, we may say that the zinc rod is the negative electrode (*anode*) where oxidation takes place and the copper rod is the positive electrode (*cathode*) where reduction occurs.

This is how electrical energy is produced out of a redox reaction. The reaction and the resultant flow of current will go on until the entire zinc rod is used up or all the copper present in the copper sulphate solution is deposited. We have seen that, through the external circuit, the electrons flow from the negative to the positive pole (from Zn-rod to the Cu-rod), *i.e.* from the anode to the cathode.

In representing galvanic cells, the convention followed is to place the anode on the left and the cathode on the right. Thus, the Daniel cell may be represented as :

$$\overset{-}{Zn} \mid Zn^{+2}(aq.) \parallel Cu^{+2}(aq.) \mid \overset{+}{Cu}$$

In the left-half of the cell, reaction (a), which is an oxidation process, occurs, whereas in the right-half, reduction in the form of reaction (b) takes place. This is why (a) and (b) are called the *half-cell reactions*, *half-reactions* or *electrode-reactions*.

Examples of other such cell are :

$$\overset{-}{Cu} \mid Cu^{+2}(aq.)\ conc.C_1 \parallel (aq.)\ conc.C_2\ Ag^+ \mid \overset{+}{Ag}$$

and $\overset{-}{Zn} \mid Zn^{+2}(aq.) \parallel Hg_2^{+2}(aq.) \mid \overset{+}{Hg}$.

**Measurement of e. m. f. of cells.**

The e.m.f. of a cell is measured with the help of a pontentiometer operating on the Pogendorff compensated principle. Circuit diagram of the experiment is given in fig. 6.2.

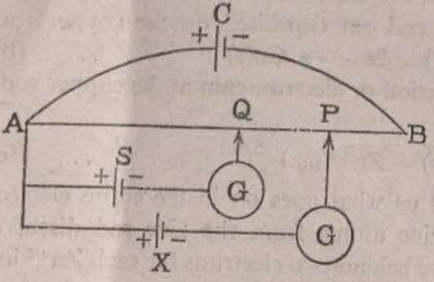


Fig 6.2

AB is the potentiometer wire of known length and high resistance. The positive pole of the cell C (whose e.m.f. is to be measured) is connected to the terminal A of the potentiometer and the negative pole is connected to the terminal B, so that potential drops from A to B. A standard cell X, whose e.m.f. is accurately known (usually a

Weston cadmium cell of e.m.f. 1.01845 volts) is also connected to the potentiometer terminals A and B, so that the e.m.f. of X opposes that of the cell C, *i.e.*, the + ve terminal of X is connected to A and the − ve terminal is connected to the sliding contact P through a sensitive galvanometer G. If Ec and Ex represent the e.m.f. of the unknown cell and the standard cell respectively, then to find Ec, current is allowed to flow through the circuit and the sliding contact is moved along the wire AB until the galvanometer shows no deflection, say, with the sliding contact at P. Under these conditions, Ec is proportional to the resistance of the portion of wire AB and Ex is proportional to the resistance of the wire AP,

*i.e.*, $$\frac{E_c}{E_x}=\frac{AB}{AP} \quad \cdots \quad \cdots \quad \cdots \quad (6.3)$$

Since Ex is known and AB and AP can be easily measured, Ec can be calculated.*

Like every other spontaneous dynamic process, the driving force of a spontaneous chemical reaction results from the tendency of the system to approach equilibrium. From the thermodynamic point of view, the tendency or urge of a chemical reaction to reach equilibrium is measured by the change in *free energy* (F) of the system in going from the initial state to the final state. If the total free energy, $F_1$, of the reactants *decreases* to $F_2$, the total free energy of the products, *i.e.*, if $F_1 > F_2$ or $(F_2 - F_1) = \Delta F$, is negative, then only the reaction will occur spontaneously. Thus, the decrease in free energy of a system is a measure of the *useful work* available from the given system under the experimental conditions. By *useful work* we mean that part of the total work done which can be utilised for practical purposes.

Again, there must be a connection between the free energy change ($\Delta F$) of a chemical reaction and its equilibrium constant (K), since, the value of the equilibrium constant tells us how far the reaction has proceeded. Under the conditions when all the reactants and the products are in their standard states, *i.e.*, when all the individual reactants and products are at *unit activity*, the relation between $\Delta F^\circ$ and K of a chemical reaction is given by the relation

$$\Delta F^\circ = RT \ln K + RT \ln \frac{a_{\text{products}}}{a_{\text{reactants}}}$$
$$= RT \ln K,$$

where $\Delta F^\circ$=free energy change under standard conditions and K is the equilibrium constant of the reaction being considered and T is the temperature of the reaction in the absolute scale ; $a_{\text{reactants}}$ and $a_{\text{products}}$ represent the activity terms, $\ln \frac{a_{\text{products}}}{a_{\text{reactants}}}$ becoming zero under unit activity conditions.

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*In this method $E_C$ has to be greater than $E_X$.

Again, for a spontaneous chemical reaction,

$$aA+bB+\ldots \rightleftharpoons lL+mM+\ldots,$$

the free energy change is given by,

$$\Delta F = \Delta F^\circ + RT \ln \frac{(a_L)^l+(a_M)^m \ldots}{(a_A)^a+(a_B)^b \ldots} \quad \ldots \quad (6.4)$$

where the '*a*' terms represent the activity of the species present. From the above equation, it is clear that, under standard conditions, all the terms of the ratio $(a_L)^l+(a_M)^m/(a_A)^a+(a_B)^b$ are equal to unity, making the ratio itself equal to unity. Thus, in the standard state,

$$\Delta F = \Delta F^\circ.$$

At this point, we focus our attention again on electrochemical cells. In an electrochemical cell, the energy of the chemical reaction (a redox reaction, to be more precise) is converted into electrical energy. When the two electrodes of a cell are connected externally by an electronic conductor, electricity flows through the circuit, performing some electrical work. The magnitude of this electrical work is given by *n*.F.E., when the e.m.f. of the cell being considered is E volts, and the redox process occuring in the cell is accompanied by the passage of *n* Faraday of electricity, or *n*.F coulombs of electric charge. Since, this electrical work is the result of the decrease in the free energy of the reaction taking place inside the cell, we have,

$$\Delta F = -nFE.^*$$

Under standard conditions, the above equation can be written as

$$\Delta F^\circ = -nFE,$$

where E°=e.m.f. of the cell in the standard state. Now, putting $-nFE$ for $\Delta F$ and $-nFE^\circ$ for $\Delta F^\circ$ in eqn. 6.4, we get,

$$-nFE = -nFE^\circ + RT \ln \frac{(a_L)^l+(a_M)^m \ldots}{(a_A)^a+(a_B)^b \ldots}$$

$$\text{or} \quad E = E^\circ - \frac{RT}{nF} \ln \frac{(a_L)^l+(a_M)^m \ldots}{(a_A)^a+(a_B)^b \ldots}$$

$$= E^\circ + \frac{RT}{nF} \ln \frac{(a_A)^a+(a_B)^b \ldots}{(a_L)^l \times (a_M)^m \ldots} \quad \ldots \quad \ldots \quad (6.5)$$

Here '*n*' is the number of moles of electrons involved in the cell-reaction. This is one form of the Nernst equation and it relates the experimental e.m.f. (E) of an electrochemical cell, its e.m.f. in the standard state (E°) and the activities of the reactants and the products of the reaction. This equation has wide applicability in electrochemistry and we will later consider its application in the field of redox phenomenon in analytical chemistry.

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*This work is negative because negative charge moves.

## ELECTRODE POTENTIALS.

Since most of the redox reactions can be visualised as taking place at the electrodes of suitably designed electrochemical cells, we will now focus our attention on the potentials of individual electrodes or *single electrodes* at which the *half-reactions* actually take place, and utilise the Nernst equation to calculate the potentials of the single electrodes.

Whenever a metal is immersed in a solution containing its own ions, a potential difference is set up between the two. If we represent the electrode reaction by $M^{+n}+ne \rightleftharpoons M$, then by applying the Nernst equation (6.5), the electrode potential E is found as

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{M^{+n}}}{a_M} \qquad \cdots \qquad \cdots \qquad (6.6)$$

Here, $M^{+n}$ is the oxidised form and M is the reduced form of the species undergoing redox reaction at the electrode. So, we can write, $E = E^\circ + \frac{RT}{nF}\ln\frac{[Ox]}{[Red]}$.

Again $a_M$, the activity of the pure metal, is equal to unity according to convention. Thus, the eqn. 6.6 now becomes,

$$E = E^\circ + \frac{RT}{nF} \ln a_{M^{+n}} \qquad \cdots \qquad \cdots \qquad (6.7)$$

where E is the observed potential of the electrode and is known as the *single electrode potential*, R=the universal gas constant, T=temperature (in °K) of the experiment, F=Faraday, $a_{M^{+n}}$=activity of the metal ion in solution, and may be replaced by the corresponding concentration, $c_{M^{+n}}$, in dilute solution.

If the solution is so prepared that the activity of the $M^{+n}$ ions be equal to unity, then the eqn. 6.7 reduces to $E = E^\circ$. Thus, E° is the potential of an electrode when it is in equilibrium with its own ions in a solution of unit activity. E° is called **the standard electrode potential.** Larger values of E°denote greater tendency of the metal to lose electrons, *i.e.*, greater electropositive character. Thus, **the magnitude of the standard electrode potential is a measure of the electropositive or metallic character.**

The potential of a single electrode can be calculated, if a second electrode of known potential, called a **reference electrode** (say, a normal calomel or normal hydrogen electrode) is combined with it to make a complete cell whose e.m.f. can be measured. Since the e.m.f. of a cell is the algebraic sum of the potentials of the single electrodes constituting the cell, knowing the electrode potential of the reference electrode and the measuring the E.M.F. of the complete cell, the single electrode potential can be calculated. The ultimate standard of comparing electrode potentials is the **normal hydrogen electrode,** whose potential is taken to be **zero.**

## SIGN OF THE ELECTRODE POTENTIALS.

The European and the American scientists use different signs for the standard electrode potentials, and this causes a lot of confusion among the students who read both American and European books. However, the confusion may be overcome by noting that, **according to the present international convention, the sign of the electrode potential is the same as that of the electrostatic charge on the electrode.** Thus, with respect to the standard hydrogen electrode, the $Zn/Zn^{+2}$ electrode in the Daniel cell has a negative potential, while the sign of the potential of the $Cu/Cu^{+2}$ electrode is positive.

When metals are arranged in a series in the order of their standard electrode potentials, we obtain the so-called **electrochemical series of metals.** Table 6.2 includes the E° values at 25°C of some of the more common metals.

TABLE 6.2

| System | E° Volts at 25°C | System | E° volts at 25°c |
|---|---|---|---|
| | | $Fe^{+2}/Fe$ | −0.44 |
| $Li^{+}/Li$ | −3.05 | $Cd^{+2}/Cd$ | −0.40 |
| $K^{+}/K$ | −2.93 | $Co^{+2}/Co$ | −0.27 |
| $Ba^{+2}/Ba$ | −2.90 | $Ni^{+2}/Ni$ | −0.23 |
| $Sr^{+2}/Sr$ | −2.89 | $Sn^{+2}/Sn$ | −0.14 |
| $Ca^{+2}/Ca$ | −2.84 | $Pb^{+2}/Pb$ | −0.13 |
| $Na^{+}/Na$ | −2.71 | $H^{+}/\frac{1}{2}H_2$ | 0.00 |
| $Mg^{+2}/Mg$ | −2.37 | $Cu^{+2}/Cu$ | +0.35 |
| $Al^{+3}/Al$ | −1.66 | $Hg^{+2}/Hg$ | +0.79 |
| $Mn^{+2}/Mn$ | −1.08 | $Ag^{+}/Ag$ | +0.80 |
| $Zn^{+2}/Zn$ | −0.76 | $Au^{+3}/Au$ | +1.38 |

As already mentioned, the potential values given in table 6.2 are with respect to the potential of the normal hydrogen electrode taken as zero. A negative potential value indicates that the metal has a greater tendency to be oxidised into its ions than that of the metal ion to be reduced. Thus, if a metal with a negative potential value is put in a solution containing $H^+$ ions, it will lose electron(s) and will be converted into its own ions, and the electron(s) released by it will be accepted by the $H^+$ ions, forming hydrogen gas. Hence, all metals with negative potentials will liberate hydrogen from solutions containing $H^+$ ions (or from acids). On the other hand, a positive potential value indicates a greater tendency on the part of the metal ion to be reduced, than the tendency of the metal to be oxidised to its ions. Thus, metals with positive potentials will not liberate hydrogen from a solution containing $H^+$ ions, *i.e.* from acidic solutions. This is why Cu, Hg, Ag and Au do not dissolve in acids like HCl, $H_2SO_4$ (non-oxidising acids) under ordinary conditions, while most of the metals having negative E° values easily dissolve in them, liberating hydrogen gas. It must be noted here that, *a system having a higher negative potential value will displace a system having a lower negative potential from its solution.*

**Strength of oxidising and reducing agents in conjugate oxidant-reductant pairs.**

An oxidant takes up electrons, forming the reductant :

$$\underset{\mathbf{Ox_1}}{M^{+n}+ne} \rightleftharpoons \underset{\mathbf{Red_1}}{M}$$

The more easily the oxidant takes up electrons, the less energetically the conjugate reductant gives them up, *i.e.* stronger the oxidant, the weaker is the conjugate reductant. In the redox system, $F+e \rightleftharpoons F^-$, F is a very strong oxidant and so, $F^-$ is a very weak reducing agent. In the system, $Sn^{+4}+2e \rightleftharpoons Sn^{+2}$, $Sn^{+2}$ is a fairly strong reducing agent, while the $Sn^{+4}$ is a weak oxidising agent. This reminds us of the conjugate acid-base relationship involved in the neutralisation reaction.

$$Acid_1+Base_2 \rightleftharpoons Acid_2+Base_1.$$

## OXIDATION-REDUCTION POTENTIAL OR REDOX POTENTIAL.

The redox potential is the parameter which enables us to evaluate and classify the oxidising and the reducing power of different systems. Let a redox system be represented by the general expression, $\mathbf{Ox}+ne \rightleftharpoons \mathbf{Red}$, where **Ox** is the oxidising species and **Red** is its reduced form. The observed potential (E) of the half-cell due to the above reaction is given by,

$$E = E^\circ+\frac{RT}{nF}\ln\frac{[Ox]}{[Red]} \quad \cdot\cdot \quad (6.8)$$

The observed potential E controls the exchange of electrons. The potential E can be actually generated and measured by constructing an appropriate cell, in which the above reaction takes place. The electrodes used must be inert, *i.e.*, the material of the electrodes must not be oxidisable. [If so, it will send its own ions in the solution, releasing electrons which are not included in the system, $Ox + ne \rightleftharpoons Red$.] The sole purpose of these inert electrodes is to mediate the circulation of the electrons already present in solution, belonging only to the system in operation. Platinum and gold are suitable as electrode materials, as they are not oxidisable under ordinary conditions.

In the experimental determination of the redox potential of any system, it must be remembered that the value of the potential depends on the strengths of the oxidising and the reducing agents, as well as on their relative concentrations. Thus, if we want to compare the strengths of the oxidising and reducing agents, we must work under conditions where the concentrations will be equal, *i.e.* $[Ox]=[Red]$. Under this standard condition, eqn. 6.8 reduces to $E = E^\circ$, where $E^\circ$ is known as the **normal potential of the system.** Hence, the normal potential of a redox system is defined as the potential of an inert electrode (say, platinum) immersed in a solution containing equal concentrations (more accurately, equal activities) of both the oxidised and the reduced forms, measured against a normal hydrogen electrode. Normal potentials of some important redox systems, often required in the practical field, are listed in Table 6.3.

TABLE 6.3

*Normal potentials* ($E^\circ$) *of some red-ox systems* (Hydrogen scale)

| Electrode | Electrode reaction | Electrode potential $E^\circ$ (volts) |
|---|---|---|
| (Pt) $Cr^{+3}/Cr^{+2}$ | $Cr^{+3}+e \rightleftharpoons Cr^{+2}$ | −0.41 |
| (Pt) $V^{+3}/V^{+2}$ | $V^{+3}+e \rightleftharpoons V^{+2}$ | −0.21−0.25 |
| (Pt) $H^+/\frac{1}{2}H_2$ | $H^+ + e \rightleftharpoons \frac{1}{2}H_2$ | 0.00 |
| (Pt) $Sn^{+4}/Sn^{+2}$ | $Sn^{+4}+2e \rightleftharpoons Sn^{+2}$ | +0.15 |
| (Pt) $Cu^{+2}/Cu^{+1}$ | $Cu^{+2}+e \rightleftharpoons Cu^{+1}$ | +0.16 |
| (Pt) $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ | $Fe(CN)_6^{3-}+e \rightleftharpoons Fe(CN)_6^{4-}$ | +0.36 |
| (Pt) $MnO_4^-/MnO_4^{2-}$ | $MnO_4^-+e \rightleftharpoons MnO_4^{2-}$ | +0.54 |
| (Pt) $\frac{1}{2}I_2/I^-$ | $\frac{1}{2}I_2+e \rightleftharpoons I^-$ | +0.535 |
| (Pt) $Fe^{+3}/Fe^{+2}$ | $Fe^{+3}+e \rightleftharpoons Fe^{+2}$ | +0.77 |
| (Pt) $\frac{1}{2}Br_2/Br^-$ | $\frac{1}{2}Br_2+e \rightleftharpoons Br^-$ | +1.065 |
| (Pt) $IO_3^-/\frac{1}{2}I_2$ | $IO_3^-+6H^++5e \rightleftharpoons \frac{1}{2}I_2+3H_2O$ | +1.20 |
| (Pt) $MnO_2/Mn^{+2}$ | $MnO_2+4H^++2e \rightleftharpoons Mn^{+2}+2H_2O$ | +1.23 |
| $Tl^{+3}/Tl^{+1}$ | $Tl^{+3}+2e \rightleftharpoons Tl^{+1}$ | +1.25 |
| $\frac{1}{2}Cl_2/Cl^-$ | $\frac{1}{2}Cl_2+e \rightleftharpoons Cl^-$ | +1.36 |
| $Cr_2O_7^{2-}/2Cr^{+3}$ | $Cr_2O_7^{2-}+14H^++6e \rightleftharpoons 2Cr^{+3}+7H_2O$ | +1.36 |
| $MnO_4^-/Mn^{+2}$ | $MnO_4^-+8H^++5e \rightleftharpoons Mn^{+2}+4H_2O$ | +1.52 |
| $BrO_3^-/\frac{1}{2}Br_2$ | $BrO_3^-+6H^++5e \rightleftharpoons \frac{1}{2}Br_2+3H_2O$ | +1.52 |
| $Ce^{+4}/Ce^{+3}$ | $Ce^{+4}+e \rightleftharpoons Ce^{+3}$ | +1.61 |
| $MnO_4^-/MnO_2$ | $MnO_4^-+4H^++3e \rightleftharpoons MnO_2+2H_2O$ | +1.69 |
| $Co^{+3}/Co^{+2}$ | $Co^{+3}+e \rightleftharpoons Co^{+2}$ | +1.82 |
| $S_2O_8^{2-}/2SO_4^{2-}$ | $S_2O_8^{2-}+2e \rightleftharpoons 2SO_4^{2-}$ | +2.01 |
| $\frac{1}{2}F_2/F^-$ | $\frac{1}{2}F_2+e \rightleftharpoons F^-$ | +2.65 |

In the above table, the systems above the $H^+/\frac{1}{2}H_2$ system are stronger reducing agents than hydrogen, and the reducing power increases upwards, *i.e.* the higher the negative value of E°, greater is the reducing strength of the system. In a similar manner, the systems having positive potentials are stronger oxidising agents than the $H^+$ ion. **Larger the positive value of E° of a system, greater is its power as an oxidising agent.** Another very important conclusion can be drawn from the E° values given in the above table. The oxidised form of a system with a higher positive E° value will oxidise the reduced form of a system with a lower positive E° value. Thus, $Fe^{+3}$ (E° of $Fe^{+3}/Fe^{+2}$ system$=+0.77$) oxidises $Sn^{+2}$ (E° of $Sn^{+4}/Sn^{+2}$ system$=$ $+0.15$V) to $Sn^{+4}$, itself being reduced to $Fe^{+2}$. This phenomenon can also be described in the reverse manner. The reduced form of a system having lower positive potential (or higher negative potential) will reduce the oxidised form of a system having higher positive potential (or lower negative potential). Thus, $Sn^{+2}$ reduces $Fe^{+3}$ to $Fe^{+2}$, itself being oxidised to $Sn^{+4}$.

In the Table 6.2, which includes the single electrode potentials of some of the more common metals, the E° values indicate that the alkali and the alkaline earth metals are the strongest reducing agents. The data in Table 6.3 tells us that, $F_2$ is the strongest oxidising agent enlisted there. The other stronger oxidising systems used for common practical purposes are : $IO_3^-/\frac{1}{2}I_2$, $\frac{1}{2}Cl_2/Cl^-$, $Cr_2O_7^{2-}/2Cr^{+3}$, $MnO_4^-/Mn^{+2}$, $BrO_3^-/\frac{1}{2}Br_2$, $Ce^{+4}/Ce^{+3}$ and $S_2O_8^{2-}/2SO_4^{2-}$.

### FORMAL POTENTIAL.

The normal potentials (E°) are calculated with respect to the activity of both the oxidised and the reduced forms, assuming them to be present in the simple forms represented in the electrode reactions. But, in actual cases, concentrations and activities are not generally equal, and depending on experimental conditions, the participating ions may not be present as simple aquo-ions (since most common redox reactions take place in aqueous medium). A considerable portion of them may be present as different complex species, which results in the change in the activities or concentrations of the species involved in the red-ox reaction being considered. But, these effects generally affect the oxidised and the reduced forms to different extents, which results in the increase or decrease of the ratio [Ox]/[Red]. Thus, under ordinary experimental conditions, normal potentials are seldom attained and hence are not fully applicable in practice. To overcome this difficulty, normal potentials are replaced by the more useful

**formal potentials.** The formal potential of a redox system is the experimentally determined potential of a solution, in which the formal concentrations of both the oxidised and the reduced forms are equal, and it includes the effects of the other ions that are present in the reaction-medium. By a 1-formal (1F) solution of a compound, we mean a solution which contains one *formula-weight* of the compound per litre. So, one litre of a 1F solution of $FeSO_4$ contains one formula-weight of ferrous sulphate. The following table (Table 6.4) includes the formal potentials of a few common redox systems (under different experimental conditions), along with their normal or standard potentials, in order to emphasise the importance of the formal potential concept in practical field.

TABLE 6.4

| Redox system | Normal potentials (volts at 25°C) | Formal potentials (volts at 25°C) |
|---|---|---|
| $Fe^{+3}/Fe^{+2}$ | $+0.77$ | $+0.73$ in 1M $HClO_4$ |
| | | $+0.70$ in 1M HCl |
| | | $+0.68$ in 1M $H_2SO_4$ |
| | | $+0.61$ in 0.5M $H_3PO_4+1M\ H_2SO_4$ |
| $Ce^{+4}/Ce^{+3}$ | $+1.45$ | $+1.44$ in 1M $H_2SO_4$ |
| | | $+1.61$ in 1M $HNO_3$ |
| | | $+1.70$ in 1M $HClO_4$ |
| $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ | $+0.36$ | $+0.71$ in 1M $HCl/H_2SO_4/HClO_4$ |

## FACTORS INFLUENCING THE POTENTIALS OF REDOX SYSTEMS.

The most important factors which affect the E-value of many redox systems and create the necessity of introducing the **formal potential concept** are : (i) precipitation of either the oxidised or the reduced form, (ii) complex formation and (iii) pH of the reaction-medium.

### (i) Change in the redox potential of a system due to the precipitation of either the oxidised or the reduced form.

The expression for the observed potential (E) of a redox system, $Ox+ne \rightleftharpoons Red$, given by $E = E^\circ + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]}$, indicates that, E is dependent on the ratio $\frac{[Ox]}{[Red]}$. So, if any one of [Ox] or [Red] is changed, the value of E will change. Thus, if the concentration of the oxidised form is decreased by precepitation of this form from the solution, the observed value of E will decrease, since [Ox] is in the numerator. Again, if the reduced form is removed from the sphere of reaction by precipitation, the magnitude of the [Red] term will decrease, and as it occurs in the denominator, this effect will result in the increase of the observed value of E. The magnitude of such an increase will depend on the amount of the reduced form, *i.e.* on the [Red] still remaining in solution. In other words, it will depend upon the solubility of the precipitate under the experimental conditions. Sometimes, it may so happen that, as a result of such a decrease in the [Red] term due to precipitation, the potential of a redox system with lower positive value may be increased to such an extent that it will oxidise another system with a higher E° value. We are familiar with the iodometric determination of copper in volumetric analysis. The estimation is based on the reaction, $2Cu^{++}+4I^- = Cu_2I_2(\downarrow)+I_2$. This reaction involves the systems

$Cu^{++}/Cu^+$ of $E^\circ=+0.16V$ and $\frac{1}{2}I_2/I^-$ of $E^\circ=+0.535V$.

These E°-values suggest that the reaction should occur as

$$Cu^{+1}+\tfrac{1}{2}I^\circ_2 \rightleftharpoons Cu^{+2}+I^-$$

$$\text{or,}\quad Cu_2I_2+I_2 \rightleftharpoons 2CuI_2.$$

But, in practice, this never happens, and the reverse reaction takes place. This discrepancy between the expected course of the reaction based on normal potentials and the observed direction of the same, is due to the low solubility of $Cu_2I_2$, so that the $[Cu^+]$ is much lowered and the observed potential of the $Cu^{+2}/Cu^{+1}$ system becomes considerably high. In such iodometric estimations, $I^-$ ion is added in excess. If we assume that $[I^-]$ in such a solution be $10^{-1}$ gm-ion/litre, then, the solubility product of cuprous iodide, $K_s=[Cu^+]+[I^-]$ being $10^{-12}$,

$$[Cu^+]=\frac{10^{-12}}{[I^-]}=\frac{10^{-12}}{10^{-1}}=10^{-11}.$$

Putting this value of $[Cu^+]=10^{-11}$ in the expression for E of the $Cu^{+2}/Cu^+$ system, we get,

$$E=+0.16+\frac{RT}{nF}\ln\frac{[Cu^{+2}]}{10^{-11}}=0.16+2.303\frac{RT}{nF}\log\frac{Cu^{+2}}{10^{-11}}\cdot$$

Here, $n=1$ and at 20°C, $2.303\ \frac{RT}{F}=0.059$.

$$\therefore\quad E=0.16+0.059\log[Cu^{+2}]-0.059\times(-11)$$
$$=0.809+0.059\log[Cu^{+2}]$$

Since 0.809V is greater than 0.535V, the E° value for $\frac{1}{2}I_2/I^-$ system, $Cu^{+2}$ will oxidise $I^-$, liberating iodine.

(ii) **Change in the redox potential of a system due to complex formation.**

The observed potential of a redox system is sometimes profoundly affected by complex formation. The E° value of the system $Co^{+3}+e \rightleftharpoons Co^{+2}$, is 1.82 volts and hence, $Co^{+3}$ is a very strong oxidising agent. Thus, $Co^{+2}$ is a very weak reducing agent and cannot be directly titrated against the common and fairly strong oxidising agents like ceric sulphate, permanganate *etc.* But, cobalt (II) can be titrated with $Ce^{+4}$ (E° of $Ce^{+4}/Ce^{+3}=1.61$) in the presence of the complexing agent EDTA (ethylenediamine tetraacetic acid). This is possible because the complexing agent (EDTA) forms complexes with both $Co^{+2}$ and $Co^{+3}$, but the complex with $Co^{+3}$ is much stronger, as a result of which the concentration of $Co^{+3}$ is considerably decreased. Since the $[Co^{+3}]$ occurs in the numerator of the expression for the electrode potential of the $Co^{+3}/Co^{+2}$ system, the large decrease of $[Co^{+3}]$ results in profound decrease of the observed potential of the system, which becomes nearly 0.60 volts. Now, this is much lower than the E° of $Ce^{+4}/Ce^{+3}$ and hence $Co^{+2}$ can be smoothly titrated with $Ce^{+4}$ in presence of EDTA.

(iii) **The change in redox potential of a system due to change in hydrogen-ion concentration or pH of the reaction medium.**

If the redox system involves $H^+$, it is quite evident that the potential of the system will depend on the pH of the medium. For example, if we consider the redox system, $Cr_2O_7^{2-}+14H^++6e \rightleftharpoons 2Cr^{+3}+7H_2O$, we can write,

$$E = 1.36+\frac{RT}{nF}\ln\frac{[Cr_2O_7^{2-}]\,[H^+]^{14}}{[Cr^{+3}]^2},\quad (E^\circ \text{ for } Cr_2O_7^{2-}/Cr^{+3}=1.36).$$

It is clear from the above expression that, even a small change in $[H^+]$ greatly affects the $\frac{[Cr_2O_7^{2-}]\ [H^+]^{14}}{[Cr^{+3}]^2}$ ratio, and hence changes the observed E value considerably.

The tremendous influence of $[H^+]$ (and hence of pH) on the course of redox reactions involving $H^+$ can be illustrated by the reaction of $NO_2^-$ and $I^-$ in aqueous solution. When a nitrite like $NaNO_2$ is added to an aqueous solution of an iodide, no reaction takes place. However, if a small quantity of an acid like HCl, $H_2SO_4$ *etc.* is added to the mixture in solution, violent reaction starts and iodine is liberated according to the reaction, $2NO_2^-+2I^-+4H^+ \rightleftharpoons 2NO\uparrow+I_2+2H_2O$.

The potentials of all the redox systems which involve either $H^+$ or $OH^-$ ions are more or less affected by the change in $[H^+]$ of the reaction medium.

All the cases discussed above under the headings (i), (ii) and (iii) definitely establish **the utility of the formal potential concept**.

## APPLICATIONS OF REDOX POTENTIALS.

### 1. Prediction of reactions.

(*a*) Of two redox couples, the one with a higher positive E° value will oxidise the other with a lower positive $E_0$ value. (*b*) *Conversely*, a system with a lower positive potential or higher negative potential value will reduce the others with lower negative potentials or higher positive potentials respectively. As an illustration, we may consider the following two couples :

$$\text{(i)}\ Fe^{+3} + e \rightleftharpoons Fe^{+2}, \quad E^\circ = 0{\cdot}77V$$

$$\text{(ii)}\ Sn^{+4} + 2e \rightleftharpoons Sn^{+2}, \quad E^\circ = 0{\cdot}15V.$$

We know that the reaction, $2Fe^{+3} + Sn^{+2} \rightleftharpoons 2Fe^{+2} + Sn^{+4}$, occurs spontaneously. Thus, we find that $Fe^{+3}$, the oxidised form of the couple (i) with higher positive $E_0$ value, oxidises the reduced form, $Sn^{+2}$, of the couple (ii) having the lower positive E° value. We can express this behaviour in a different manner by saying that, the reduced form of the couple with lower positive potential ($Sn^{+2}$) reduces the oxidised form ($Fe^{+3}$) of the couple with higher positive potential.

But, while drawing such conclusions, it must be kept in mind that the normal potential data, E°s of the systems are to be used with reserve and restraint. We have already seen that, depending on experimental conditions, and also due to the effects of precipitation, complex-formation and change in $[H^+]$, the potentials of some systems differ considerably from their reported normal potentials.

### 2. Calculation of equilibrium constants of redox reactions.

Let us consider the redox reaction, $Fe^{+2}+Ce^{+4} \rightleftharpoons Fe^{+3}+Ce^{+3}$. We will now calculate the equilibrium constant of this reaction from the E° data of the two interacting systems.

$$\text{Here, } K = \frac{[Fe^{+3}] \times [Ce^{+3}]}{[Fe^{+2}] \times [Ce^{+4}]}$$

The individual electrode reactions are :

$$Fe^{+3}+e \rightleftharpoons Fe^{+2} \text{ and } Ce^{+4}+e \rightleftharpoons Ce^{+3}$$

Thus, we can write

$$E_{Fe^{+3}/Fe^{+2}}=0{\cdot}77+0{\cdot}059\log\frac{[Fe^{+3}]}{[Fe^{+2}]}$$

$$\text{and } E_{Ce^{+4}/Ce^{+3}}=1{\cdot}61+0{\cdot}059\log\frac{[Ce^{+4}]}{[Ce^{+3}]}$$

$$(E^\circ_{Fe^{+3}/Fe^{+2}}=0{\cdot}77V \text{ and } E^\circ_{Ce^{+4}/Ce^{+3}}=1{\cdot}61V)$$

At equilibrium, $E_{Fe^{+3}/Fe^{+2}}=E_{Ce^{+4}/Ce^{+3}}$ ; because at equilibrium, there is no driving force for the occurrence of further reaction and hence, the e.m.f. of the cell comprising the $Ce^{+4}/Ce^{+3}$ and $Fe^{+3}/Fe^{+2}$ electrodes will be zero. Thus, at equilibrium we can write,

$$1{\cdot}61+0{\cdot}059\log\frac{[Ce^{+4}]}{[Ce^{+3}]}=0{\cdot}77+0{\cdot}059\log\frac{[Fe^{+3}]}{[Fe^{+2}]}$$

$$\text{or, } 1{\cdot}61-0{\cdot}77=0{\cdot}059\log\frac{[Fe^{+3}]}{[Fe^{+2}]}-0{\cdot}059\log\frac{[Ce^{+4}]}{[Ce^{+3}]}$$

$$=0{\cdot}059\log\frac{[Fe^{+3}]\,[Ce^{+3}]}{[Fe^{+2}]\,[Ce^{+4}]}=0{\cdot}059\log K$$

$$\text{or, } 0{\cdot}84=0{\cdot}059\log K$$

$$\text{or, } \log K=\frac{0{\cdot}84}{0{\cdot}059}=14{\cdot}2$$

$$\therefore\; K=\text{antilog of } 14{\cdot}2$$

$$=1{\cdot}58\times10^{14}.$$

The very high value of K indicates that the reaction proceeds to completion from left to right and hence, it can be utilised for the quantitative estimation of ferrous iron by a ceric salt solution.

## CALCULATION OF CELL POTENTIALS.

E.M.F. of a cell, constituted by coupling two individual electrodes, can be easily calculated from the E° values given in tables 6.1 and 6.2.

Let us calculate the potential of the Daniel cell :

$$\underset{}{Zn}\mid\underset{C=1}{Zn^{+2}(\text{soln.})}\parallel\underset{C=1}{Cu^{+2}(\text{soln.})}\mid Cu$$

From Table 6.3, we have,

$$E^\circ_{Zn^{+2}/Zn}=-0{\cdot}76V \text{ and } E^\circ_{Cu^{+2}Cu}=+0{\cdot}35V$$

Thus, the E.M.F. of the cell, $E=[0{\cdot}35-(-0.76)]V$,

$$\text{or, } E=1{\cdot}11 \text{ volts.}$$

## EQUIVALENCE-POINT OF REDOX TITRATIONS AND THE CHOICE OF REDOX INDICATORS.

Let us consider the redox reaction :

$$aOx_1+bRed_2 \rightleftharpoons aRed_1+bOx_2.$$

If the standard or normal potentials of the system, $aOx_1+ne \rightleftharpoons aRed_1$, be $E^\circ_1$ and that of the system, $bOx_2+ne \rightleftharpoons bRed_2$, be $E^\circ_2$, then the potential (E) of the whole system at the equivalence-point is given by,

$$E=\frac{bE_1^\circ+aE_2^\circ}{a+b}\ .$$

Now, let us consider the case of titration of $Fe^{+2}$ by $MnO_4^-$ in acid solution. The reactions involved are

$$\begin{array}{lll} & MnO_4^- + 8H^+ + 5e & \rightleftharpoons Mn^{+2} + 4H_2O \\ \text{and} & 5Fe^{+2} & \rightleftharpoons 5Fe^{+3} + 5e \\ \hline \end{array}$$

The overall reaction is,

$$MnO_4^-+5Fe^{+2}+8H^+ \rightleftharpoons Mn^{+2}+5Fe^{+3}+4H_2O.$$

Here, $a=1$ and $b=5$.

From table 6.3, we know that,

$$E^\circ_{Fe^{+3}/Fe^{+2}}=0{\cdot}77V \text{ and} E^\circ_{MnO^-/Mn^{+2}}=1.52V.$$

$\therefore$ The potential (E) at the equivalence-point is,

$$E=\frac{5\times 1{\cdot}52+0{\cdot}77}{1+5}=1{\cdot}39 \text{ Volts.}$$

In this way, the potential at the equivalence-point of an oxidation-reduction reaction can be calculated from the E° values of the reducing and the oxidising agents.

## REDOX INDICATORS.

Redox indicators are substances which can be **reversibly** oxidised or reduced, and have different colours in the oxidised and the reduced forms.

Let us denote the oxidised form of the indicator as $Ind_{Ox}$ and the reduced form as $Ind_{Red}$. The inter-conversion of the two forms may be represented as : $Ind_{Ox}+ne \rightleftharpoons Ind_{Red}$.

It is quite evident that the potential of such a reversible redox system can be obtained from the Nernst equation,

$$E=E^\circ_{Ind}+\frac{0{\cdot}059}{n}\log\frac{[Ind_{Ox}]}{[Ind_{Red}]},$$

where E°=standard or normal redox potential of the indicator system. Table 6.5 enlists some common redox indicators along with their E° values.

TABLE 6.5

| Indicator | Colour | | E° (V) at $[H^+]=1$ |
|---|---|---|---|
| | $Ind_{Ox}$ | $Ind_{Red}$ | |
| Neutral Red | Red | Colourless | +0·24 |
| Methylene blue | Greenish blue | Colourless | +0·53 |
| Diphenyl amine | Blue-violet | Colourless | +0·76 |
| Ba-diphenylamine sulphonate | Red-violet | Colourless | +0·85 |
| Phyenylanthranilic acid | Red-violet | Colourless | +1·08 |
| Ferroin (ortho-phenanthroline-ferrous ion) | Pale blue | Red | +1·14 |

The choice of an indicator in a redox titration is based on the value of the E° of the indicator system and the potential of the systems undergoing oxidation-reduction at the equivalence-point. When a reductant is titrated with an oxidant, the E° of the indicator must be at least 0.10—0.15 volts above the E° value of the reducing agent, but it must be considerably less than the E° of the oxidising agent. Thus, for the titration of $Fe^{+2}$ by $Cr_2O_7^{2-}$, the best indicators are phenyl anthranilic acid and ferroin. The $E^\circ_{Fe^{+2}/Fe^{+2}}$ being equal to + 0·77V, $E^\circ_{Cr_2O_7^{2-}/2Cr^{+3}}$=1·36V, the potential (E) at the equivalence-point

$$E_{eq.}=\frac{0{\cdot}77+6\times1{\cdot}36}{7}=1{\cdot}275V.^*$$

If we wish to use diphenylamine as the indicator for the titration of $Fe^{+2}$ by $Cr_2O_7^{2-}$ or by $MnO_4^-$ or by $Ce^{+4}$, we must use phosphoric acid which, by complexing $Fe^{+3}$ as colourless $[Fe(HPO_4)]^+$ species, decreases the potential of the $Fe^{+3}/Fe^{+2}$ system to 0·61V, which value is more than 0·1 volt below that of the E° of the indicator system.

---

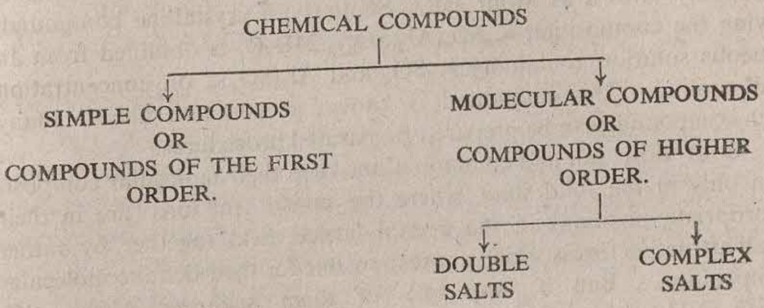
*This relation is an approximate one and can be used when high accuracy is not required. The actual relation for this system is

$$E_{eq.}=\frac{0{\cdot}77+6\times1{\cdot}36}{7}-\frac{0{\cdot}0591\log 2}{7}-\frac{0{\cdot}0591\log[Cr^{+3}]}{7}$$

CHAPTER VII

# COORDINATION COMPOUNDS AND WERNER'S THEORY

The vast number of known chemical compounds differ widely in their mode of formation, their structural characteristics and the consequent differences in properties. In a most general way, chemical compounds may be classified according to the following scheme :


CHEMICAL COMPOUNDS
SIMPLE COMPOUNDS OR COMPOUNDS OF THE FIRST ORDER.
MOLECULAR COMPOUNDS OR COMPOUNDS OF HIGHER ORDER.
DOUBLE SALTS
COMPLEX SALTS

## Simple compounds or compounds of the first order.

These compounds are formed by the union of the atoms of the elements through the operation of electrovalency or covalency. They are also formed by the action between acids and bases, or by the mutual interaction of radicals. Thus, both sodium chloride (electrovalent compound) and HCl (covalent compound) are simple compounds, which can be formed by the reaction between the elements, or for NaCl, by the neutralisation reaction between the base, NaOH and the acid, HCl. The formation of simple compounds can be explained fully by the classical concepts of electron transfer (electrovalency) or electron-pair sharing (covalency).

## Molecular compounds or compounds of the higher order.

These are formed by the combination of more than one simple compounds described above, and the *cggregates*, thus formed, are capable of *more or less* independent existence by themselves. The formation of such compounds could not be explained by the classical concepts of electrovalent and covalent bonding. The hydrates (say, $CuSO_4$,

$5H_2O$), ammoniates (say, $CuSO_4$, $4NH_3$), double-salt hydrates like alums [say, $K_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$], ferrocyanides (say, $Fe(CN)_2.4KCN$) *etc.*, belong to this class. Again, this class of compounds can be further sub-divided into *double salts* and *complex salts.*

## DOUBLE SALTS.

If one mole of ferrous sulphate and one mole of ammonium sulphate are dissolved together in water and the solution is concentrated till crystals begin to appear and then cooled, pale green crystals are obtained. There crystals correspond to the composition $FeSO_4.(NH_4)_2SO_4.6H_2O$, *i.e.*, ferrous ammonium sulphate hexahydrate, which is commonly known as Mohr salt. Similarly, a crystalline compound, having the composition $K_2SO_4.Al_2(SO_4)_3.24H_2O$, is obtained from an aqueous solution containing $K_2SO_4$ and $Al_2(SO_4)_3$, on concentration and cooling. This compound is known as common alum. Many such compounds can be prepared by parallel procedures.

Both Mohr salt and common alum keep their molecular composition only in the solid state, where the constituent ions are in their appropriate positions in the crystal lattice, held together by rather weak attractive forces which are responsible for their definite molecular composition. But, if any one of them such as Mohr salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, is put in a solvent like water, where the total solvation energy of the component ions exceeds the lattice energy of Mohr salt, it will dissolve and will break down or dissociate into the simpler constituent ions as follows :

$$FeSO_4.(NH_4)_2SO_4.6H_2O \overset{\text{water}}{\rightleftharpoons} Fe^{+2}+2NH_4^{+}+2SO_4^{2-}+6H_2O,$$

the ions being present in the solvated condition.

The existence of all these ions can be proved by performing the following chemical tests :

(1) To one part of the above solution, a little dilute $H_2SO_4$ and a few drops of potassium *ferricyanide* is added. A blue precipitate (Turnbull's blue) *indicates the presence of* $Fe^{+2}$.

(2) A portion of the solution is treated with dilute HCl and $BaCl_2$ solution. A heavy white precipitate, insoluble in all acids, *indicates the presence of sulphate ions.*

(3) Another portion of the solution is boiled with a few beads of caustic soda and the issuing gas is passed through Nessler's solution. The formation of a brown precipitate proves the *presence of the ammonium ion* in the solution. [The strong smell of ammonia, issuing

from the alkaline solution, will also indicate the presence of the $NH_4^+$ ions in solution.]

Hence, we may define a double salt as a molecular compound, formed by the union of two or more different simple compounds. They are capable of independent existence as such, only in the solid state, but dissociate *practically completely* in solution and yield *all* the constituent simple ions in solution. The process is reversible and the solution, on concentration, yields the original double salt. Some other double salts are :

1. the alums : $M_2^{II}(SO_4)_3.M_2^{I}.SO_4.24H_2O$, where $M^{II}=Al^{+3}$, $Fe^{+3}$, $Cr^{+3}$, $Mn^{+3}$ and $M^{I}=K^+$, $Rb^+$, $Cs^+$, $NH_4^+$.

2. the double sulphate hydrates :
$M^{II}SO_4.(NH_4)_2SO_4.7H_2O$, where $M^{II}=Fe^{II}$, $Ni^{II}$, $Co^{II}$.

### COMPLEX SALTS.

Just as is done in the case of the preparation of the double salt, (Mohr salt), a solution containing one mole of ferrous cyanide, $Fe(CN)_2$, and four moles of potassium cyanide, KCN, is allowed to crystallise. Pale yellow crystals are obtained, which correspond to the composition, $Fe(CN)_2.4KCN$. These crystals, on dissolution in water, do not give the tests for $Fe^{+2}$ or $CN^-$ ions. It gives the test of only one constituent, the $K^+$. It also gives the test for an altogether new $[Fe(CN)_6]^{4-}$ ion by the formation of a deep blue ppt. (Prussian blue) on addition of ferric chloride to the solution. Thus, we find that, in this case a new aggregate of $Fe^{+2}$ and $CN^-$ ions has been formed by the interaction of KCN and $Fe(CN)_2$, which is capable of keeping individual existence in solution. This new ion $[Fe(CN)_6]^{4-}$ is not dissociated into its constituents to any appreciable extent. If it had dissociated in solution, we would have obtained the tests for $Fe^{+2}$ and $CN^-$. Such an aggregate, formed by the interaction of two or more different molecules or ions, and capable of keeping independent existence in solution, is called a *coordination complex* or simply a *complex*. It may be a cation like $[Co(NH_3)_6]^{+3}$, an anion like $[Fe(CN)_6]^{4-}$ or a neutral species like $[Cr(H_2O)_3Cl_3]^{\circ}$. If the resultant complex is an ion, its charge is neutralised by a counter-ion, positive or negative, and the complete species is called a *complex salt*.

### Formation and subsequent dissociation of some complex salts in aqueous solution.

Table 7.1 shows the formation and dissociation of some familiar complex salts in solution.

TABLE 7.1

1. $AgNO_3+2NH_3 \rightleftharpoons [Ag(NH_3)_2]NO_3 \rightleftharpoons [Ag(NH_3)_2]^+ + NO_3^-$
2. $CuSO_4+4NH_3 \rightleftharpoons [Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{+2} + SO_4^{2-}$
3. $PtCl_2+2KCl \rightleftharpoons K_2[PtCl_4] \rightleftharpoons 2K^+ + [PtCl_4]^{2-}$
4. $Cr(SCN)_3+3KSCN \rightleftharpoons K_3[Cr(SCN)_6] \rightleftharpoons 3K^+ + [Cr(SCN)_6]^{3-}$
5. $Fe(CN)_2+4KCN \rightleftharpoons K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$
6. $CrCl_3+3H_2O \rightleftharpoons [Cr(H_2O)_3Cl_3]^\circ \rightleftharpoons$ no dissociation
7. $Co(SCN)_2+2KSCN \rightleftharpoons K_2[Co(SCN)_4] \rightleftharpoons 2K^+ + [Co(SCN)_4]^{2-}$

### SOME IMPORTANT TERMS.

In all the above cases, we observe that, a metal ion $M^{+n}$ (*e.g.*, $Ag^+$, $Cu^{+2}$, $Pt^{+2}$, $Cr^{+3}$ *etc.*) combines with neutral molecules (*e.g.* $NH_3$, $H_2O$ *etc.*) or anions (*e.g.*, $Cl^-$, $SCN^-$ *etc.*) to give the new polyatomic cations (cases 1, 2), the polyatomic anions (cases 3, 4, 5 and 7) and neutral polyatomic species (case 6), capable of keeping their independent existence in solution. Such polyatomic entities, included in the square brackets in the above examples, are called *complexes.* The ions or molecules closely associated with the metal ion are called *ligands.* Thus, $NH_3$, $Cl^-$, $SCN^-$, $CN^-$ *etc.* are examples of ligands. A ligand may possess one or more than one *donor sites* (or attachment sites), through which it may attach itself to one or more than one points around a metal ion. The ligands cited in Table 7.1 are all *monodentate* ones, as they occupy only one position each in the *coordination zone* (see later). The oxalate ion ($C_2O_4^{2-}$) or the ethylenediamine molecule, ($NH_2.CH_2.CH_2.NH_2$), attaches itself to a metal ion through both its carboxyl groups or the two N-atoms of the $-NH_2$ groups, and thus occupies two positions inside the coordination zone of the metal complex. These are called *bidentate* ligands. Similarly, *tridentate* ligands occupy three positions, *tetradentate* ligands occupy four positions and so on. The total number of positions occupied by the ligands present within the coordination zone of a metal complex represents the *coordination number* of the metal ion in the complex. Thus, the coordination number of Co(III) in both $[Co(NH_3)_6]Cl_3$ and $K_3[Co(C_2O_4)_3]$ is six. In $[Ag(NH_3)_2]^+$, the coordination number of $Ag^{+1}$ is 2. Similarly, in $[Cu(NH_3)_4]SO_4$, the coordination number of $Cu^{+2}$ is 4 and so on. In a complex entity $[ML_x]^{+n}$, with a monodentate ligand, L, $x$ is the coordination number of the metal ion, $M^{+n}$. In a complex compound, the portion within the square bracket, made up of the metal ion and the ligands, is called the *coordination zone* or the *first coordination sphere* of the complex. The ions (or molenles) within this zone are not appreciably dissociated in solution into the constituent ions, (or molecules), while those outside it can freely dissociate in solution. Thus, the complex compound, potassium ferrocyanide, dissociates as : $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$, but the $[Fe(CN)_6]_4^-$ ion *does not dissociate* further into $Fe^{+2}$ and $CN^-$ ions. It may be mentioned here that the ligands within the coordination zone of a metal ion are arranged in *definite geometrical patterns*, which depend on the coordination number and nature of the metal ion.

**Detection of complex-formation in solution.**

During the discussion on the preparation of double and complex salts, we have noticed that both the double salts and the complex salts are generally prepared by the similar method of mixing simple compounds in the required proportions in solution, followed by concentration and crystallisation. But, whether the preparative method had yielded a double salt or a complex salt, must be ascertained. We have already disscussed how the existence of a double salt or a complex salt can be proved by the detection of the ions produced in solution. Many other methods for the detection of complex formation in solution are available, some of which will now be mentioned in brief. In the solid state, the final proof of the existence of a complex species is presented by X-ray crystallography of the crystalline complex. However, the presence of complex ions in solution can be recognised by any one or more of the following methods :

(i) **Qualitative analysis of the species generated in solution** : Since the formation of a complex in solution leads to the formation of new species which ionizes differently from the components used in its preparation, the absence of certain ions and formation of new ones will indicate complex formation. We have already noted that, in the case of formation of $K_4[Fe(CN)_6]$ from KCN and $Fe(CN)_2$, we do not get the qualitative tests for either $Fe^{+2}$ or of $CN^-$, but get the tests for $K^+$ and an altogether new ion, $[Fe(CN)_6]^{4-}$.

(ii) **Abnormal increase in solubility** : If a sparingly soluble compound readily goes into solution by the addition of a reagent (a ligand), the cause is generally* attributed to complex formation. Thus, sparingly soluble silver cyanide, AgCN, goes into solution completely on the addition of excess of KCN solution. This is due to the formation of the complex $K[Ag(CN)_2]$, potassium argentocyanide.

(iii) **Measurement of conductivity** : We know that the conductivity of a solution depends mainly on the nature and number of ions present. Since both the number of ions and the nature of ions change due to complexation, an abrupt change in the conductivity values, on the mixing of the reactants, will indicate complex formation. Thus, a solution containing $Fe(CN)_2$ and KCN in 1 : 4 molar ratio has a conductance value much lower than what would have been the value, if $Fe(CN)_2$ (which ionises as $Fe^{+2}+2CN^-$) and 4KCN (which ionise as $4K^++4CN^-$) were present as such, without undergoing complex formation. The experimental conductance value, in this case, is indicative of the presence of 5 ions in solution which corresponds well to the ionisation of the potassium ferrocyanide complex as, $K_4[Fe(CN)_6] \rightleftharpoons 4K^++[Fe(CN)_6]^{4-}$.

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*Such abnormal solubility may also result due to the formation of weak acid from the anion.

(iv) **Measurement of transport number** : The transport number of an ion is the fraction of the total current carried by that particular ion under a fixed potential gradient. The transport number of an ion depends on the *nature* of the ion and hence, any change undergone by an ion will be indicated by the change in the value of its transport number. The drastic change in the value of the transport number of the $Fe^{+2}$ ion on addition of potassium cyanide solution to $Fe(CN)_2$ solution, indicates some sort of complexation involving $Fe^{+2}$ and $CN^-$ ions.

(v) **Determination of mol. wt.** : The value of the molecular weight in solution, determined by the measurement of a colligative property like depression of freezing point, depends on the number of particles present. Since complexation results in a change in the number of ions, an alteration in the value of molecular weight will indicate complex formation.

(vi) **Distribution method** : If a ligand and a metal ion react in solution to form a complex, the formation of the complex and its composition can be determined by measuring the partition coefficient of the complex species between two immiscible solvents.

(vii) **E.M.F. Method** : Since E.M.F. of many electrochemical cells depend on the nature and concentration of the ions present and undergoing redox reaction, the change in E.M.F. of the system due to addition of a reagent (ligand) will indicate complex formation.

(viii) **Change in colour** : In majority of cases, complex formation is accompanied by a change in colour of the solution, which sometimes, is profound in nature. Thus, the addition of ammonia to a $CuSO_4$ solution, abruptly changes the bluish green colour to deep blue, due to the formation of ammine complex. The addition of colourless KCNS solution to a solution containing light yellow $Fe^{+3}$ ions changes the colour to blood-red, due to the formation of the thiocyanato-complex of ferric iron.

**Stability of complex compounds in solution.**

Formation of a complex ion in solution, by the interaction of a metal ion $M^{+n}$ having the coordination number $x$, with a neutral monodentate ligand L, may be represented as :

$$M^{+n} + xL \rightleftharpoons [ML_x]^{+n}$$

The expression for the equilibrium constant of this complexation reaction is $K = \dfrac{C_{[ML_x]^{+n}}}{C_{M^{+n}} \times C^x_L}$.

K is called the stability constant of the complex $[ML_x]^{+n}$.

It is quite obvious that the value of K is a measure of *how far* the complexation reaction has proceeded in any particular direction. In other words, higher the value of K, greater is the stability of the complex.

If we consider the dissociation of the complex $[ML_x]^{+n}$, we can write $[ML_x]^{+n} \rightleftharpoons M^{+n} + xL$. The equilibrium constant of this dissociation reaction, $K_{inst.}$, is given by, $K_{inst.} = \dfrac{C_{M^{+n}} \times C^x_L}{C_{[ML^x]^{+n}}}$,

where $K_{inst.}$ is called the *instability constant* of the complex ion $[ML_x]^{+n}$, and greater the value of $K_{inst.}$, less is the stability of the complex. A high value of $K_{inst.}$ indicates that the complex is very unstable and is practically completely dissociated into the constituent ions. Thus, we may say that, *a double salt is a complex salt with very high instability constant value.*

**Perfect and imperfect complexes.**

Let us now consider the behaviour of the complex potassium cadmicyanide in solution, which is formed by the reaction of $Cd(CN)_2$ and KCN. The whole process may be represented as :

$$Cd(CN)_2 + 2KCN \rightleftharpoons K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN)_4]^{2-}$$

$$[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{+2} + 4CN^-$$

If $H_2S$ is passed through this solution, yellow cadmium sulphide is precipitated, indicating that free $Cd^{+2}$ ions are present in solution. This proves that the $[Cd(CN)_4]^{2-}$ dissociates into $Cd^{+2}$ and $CN^-$ as is indicated above. Such complexes, which are unable to completely retain their identities in solution, and dissociates **partially** into the constituent ions, are termed **imperfect complexes** or **associated complexes.**

We may now focuss our attention on the behaviour of potassium cuprocyanide, $K_3[Cu(CN)_4]$, in solution :

$$K_3[Cu(CN)_4] \rightleftharpoons 3K^+ + [Cu(CN)_4]^{3-}.$$

The cuprocyanide ion **does not** undergo further dissociation as

$$[Cu(CN)_4]^{3-} \rightleftharpoons Cu^+ + 4CN^-$$

to any appreciable extent. Hence, no precipitate of the black $Cu_2S$ is obtained on passing $H_2S$ gas through the solution of potassium cuprocyanide. Complex compounds, which are stable enough to retain their identity in solution, and thus undergo very little or practically no dissociation into the constituent ions, are called **perfect complexes** or **penetration complexes.**

Thus, we can conclude that, the difference between a perfect and an imperfect complex lies in the degree of dissociation of the complex compound involved, measured by the value of its **instability constant.** It must be kept in mind that, **there is no sharp boundary between the perfect complexes and the double salts, the imperfect complexes representing an intermediate state between the two.**

The following table (Table 7.2) contains the instability constants of some familiar complex ions.

TABLE 7.2

| Complex ion | Ionisation in solution | Instability constant |
|---|---|---|
| $[Hg(CN)_4]^{2-}$ | $Hg^{+2}+4CN^-$ | $40 \times 10^{-42}$ |
| $[Co(NH_3)_6]^{+3}$ | $Co^{+3}+6NH_3$ | $6.2\times 10^{-36}$ |
| $[Cu(CN)_4]^{3-}$ | $Cu^{+}+4CN^-$ | $5.0\times 10^{-28}$ |
| $[Ag(CN)_2]^-$ | $Ag^{+}+2CN^-$ | $1.0\times 10^{-21}$ |
| $[Cd(CN)_4]^{2-}$ | $Cd^{+2}+4CN^-$ | $1.4\times 10^{-17}$ |
| $[Ag(S_2O_3)_2]^{3-}$ | $Ag^{+}+2S_2O_3{}^{2-}$ | $1.0\times 10^{-13}$ |
| $[Cu(NH_3)_4]^{+2}$ | $Cu^{+2}+4NH_3$ | $2.1\times 10^{-13}$ |
| $[Ag(SCN)_2]^-$ | $Ag^{+}+2SCN^-$ | $2.0\times 10^{-11}$ |
| $[Ni(NH_3)_6]^{+2}$ | $Ni^{+2}+6NH_3$ | $1.8\times 10^{-9}$ |
| $[Ag(NH_3)_2]^+$ | $Ag^{+}+2NH_3$ | $7.2\times 10^{-8}$ |
| $[Co(NH_3)_6]^{+2}$ | $Co^{+2}+6NH_3$ | $7.8\times 10^{-6}$ |
| $[Fe(SCN)]^{+2}$ | $Fe^{+3}+SCN^-$ | $1.0\times 10^{-3}$ |

Stability of the complexes decreases ↓

From the values of the instability constants of the complexes included in the above table, it is obvious that, among them, $[Hg(CN)_4]^{2-}$ is the **most stable** and the $[Fe(SCN)^{+2}$ complex is the **least stable** or

**most labile.** It may also be noted here that, the first four complexes are perfect or penetration complexes, while the last eight complexes, starting from $[Cd(CN)_4]^{-2}$, are imperfect or associated complexes. Since we have already noted that $[Cd(CN)]_4^{2-}$ is an imperfect complex, other complexes which are even more dissociated in solution must also fall in the same category.

**Naming of coordination compounds.**

The present accepted system of naming the complex compounds is the I.U.P.A.C. system, which is based mainly on the following rules :

1. The cation is named first and then the anion. This sequence is followed irrespective of whether the complex is cationnic or anionic in nature. The name of the complex anions end with the suffix **'ate'.**

2. **The order, naming and designations for ligands :** (a) Neutral ligand molecules are named first, generally by their usual name, except for some ligands which have the following special names :

| | |
|---|---|
| $NH_3$ | ammine |
| $H_2O$ | aquo |
| CO | carbonyl |
| NO | nitrosyl |
| $N_2$ | dinitrogen |
| $O_2$ | dioxygen |

(b) Negative ligands **present inside the coordination zone,** such as halides, are called as **halo,** *i.e.*, just in the manner as they are named in the case of carbon compounds. For example :

| | |
|---|---|
| $CH_3COO^-$ | acetato |
| $Br^-$ | bromo |
| $Cl^-$ | chloro |
| $CN^-$ | cyano |
| $CNO^-$ | cyanato |
| $F^-$ | fluoro |
| $H^-$ | hydrido |
| $OH^-$ | hydroxo |
| $I^-$ | iodo |
| $NO_2^-$ | nitro |
| $O^{2-}$ | oxo |
| $O_2^{2-}$ | peroxo |
| $CNS^-$ | thiocyanato |
| $S_2O_3^{2-}$ | thiosulphato |

Most of the other ligands retain their ordinary names, but the whole name is written omitting spaces.

| Formula of the ligand | Ordinary name | Name in complexes |
|---|---|---|
| $(CH_3)_2SO$ | dimethyl sulphoxide | dimethylsulphoxide |
| $(CH_3)_2N.OCH)$ | dimethyl formamide | dimethylformamide |
| $(C_6H_5)_3P$ | triphenyl phosphine | triphenylphosphine |

(c) Groups of the same general nature (*i.e.* all negative, all neutral) are mentioned in the alphabetical order.

3. **Complexed metal ions and their oxidation numbers** : (a) In neutral or cationic complexes the usual name of the metal ion is used succeeded by **Roman numeral** within first bracket which denotes the *formal* oxidation number of the metal ion.

(b) For an anionic complex the metal is denoted by its name ending in "**ate**" followed by its formal oxidation number in parenthesis. In several cases the latin name of the metal is used, e.g. ferrate, aurate etc.

4. **Prefixes indicating number of ligands** : The presence of one, two or more ligands (or metal ions) within the coordination zone is designated by the following prefixes :

| number of ligands | prefixes |
|---|---|
| 1 | *mono* |
| 2 | di or *bis* |
| 3 | tri or *tris* |
| 4 | tetra or *tetrakis* |
| 5 | penta or *pentakis* |
| 6 | hexa or *hexakis* |
| 7 | hepta |
| 8 | octa |
| 9 | nona or *ennea* |
| 10 | deca |
| 11 | undeca |
| 12 | dodeca |

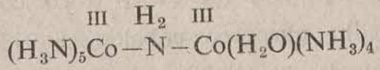
The following table (Table 7.3) contains the formula and the corresponding names of some complexes.

TABLE 7.3

| Formula | I.U.P.A.C. Name |
|---|---|
| $[Co(NH_3)_6]Cl_3$ | Hexammine cobalt (III) chloride |
| $[Co(NH_3)_5H_2O]Cl_3$ | Aquopentammine cobalt (III) chloride |
| $[Co(NH_3)_4Cl_2]^+$ | Dichlorotetrammine cobalt (III) ion |
| $[Pt(NH_3)_2Cl_4]$ | Tetrachloro diammine platinum (IV) |
| $K_4[Cr(C_2O_4)_3]$ | Potassium trioxalatochromate (III) |
| $K_4[Fe(CN)_6]$ | Potassium hexacyanoferrate (II) |
| $[Co(en)_3]Cl_3$ | Tris (ethylenediamine) cobalt (III) chloride |
| $[Cr(NH_3)_6][Co(CN)_6]$ | Hexammine chromium (III) hexacyano cobaltate (III) |
| $[Co(NH_3)_5CO_3]Cl$ | Pentammine carbonato cobalt (III) chloride |
| $[Cr(H_2O)_4Cl_2]Cl$ | Tetraaquo dichloro chromium (III) chloride |
| $[(C_6H_5)_4As][PtCl_2HCH_3]$ | Tetraphenylarsonium dichlorohydridomethyl platinate (II) |
| $[Co(NH_3)_5S_2O_3]Cl$ | Pentammine thiosulphato cobalt (III) chloride |
| $[Co(NH_3)_3(NO_2)Cl(CN)]$ | Triammine chloro cyano nitro cobalt (III) |
| $[Pt(py)_4[[PtCl_4]$ | Tetrapyridin platinum (II)- tetrachloro platinate (II) |
| $[Ni(DMG)_2]$ | *Bis*-dimethylglyoximato nickel (II) |
| $[Cr(acac)_3]$ | *Tris*-acetylacetonato chromium (III) |

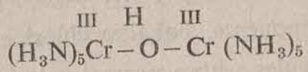
5. **Designation of bridging ligands** : A bridging ligand, spanning two metal ion centres, is designated by the prefix μ. When two identical bridging groups are present in a complex the prefix *di*-μ is used. Ordering of bridging ligand follow the same rule applicable to ordinary ligands. Some common examples are given below.

Pentammine cobalt (III)-μ-amido-tetramineaquo cobalt (III)

I. 

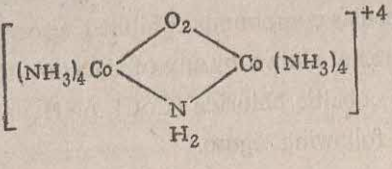
$$(H_3N)_5\overset{\text{III}}{Co}-\overset{H_2}{N}-\overset{\text{III}}{Co}(H_2O)(NH_3)_4$$

μ-hydroxo*bis* [pentammine chromium (III)

II. 

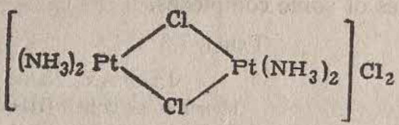
$$(H_3N)_5\overset{\text{III}}{Cr}-\overset{H}{O}-\overset{\text{III}}{Cr}\ (NH_3)_5$$

Tetrammine cobalt (III)-μ-superoxo-μ-amido-tetrammine cobalt (III)

III. 

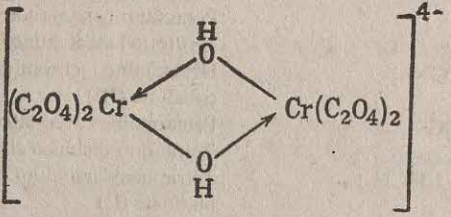
Di-μ- chlorobis [diammine platinum (II) chloride

IV.



Bis oxalato chromium (III)-μ-dihydroxobis oxalato chromium (III)

V.



### What holds the constituents of a complex together—the nature of linkage between the ligands and the metal ion in a complex.

From the later part of the 18th century, experimental evidences accumulated, indicating the formation of new types of molecular compounds, by the combination of simpler molecules, in which the normal valencies of the constituent atoms were already satisfied. Thus, treatment of a solution of cobalt (II) chloride with excess of ammonia and followed by oxidation, yielded solutions from which several different compounds could be obtained. These were called : Leuteo cobaltic chloride, $CoCl_3.6NH_3$ (yellow) ; roseo cobaltic chloride, $CoCl_3.5NH_3.H_2O$ (red) ; purpureo cobaltic chloride, $CoCl_3.5NH_3$ (green). Two compounds, one violet and the other green, and both corresponding to the formula $CoCl_3.4NH_3$, were also obtained. In such compounds, the components, cobaltic chloride, ammonia and water were saturated molecules whose normal valencies were already satisfied ; but even then, they combined with each other, forming stable entities. These molecular compounds exhibited altogether new sets of properties which were not shown by any of the constituents. Such new properties of leuteo cobaltic chloride ($CoCl_3.6NH_3$) are schematically shown below in the following figure.

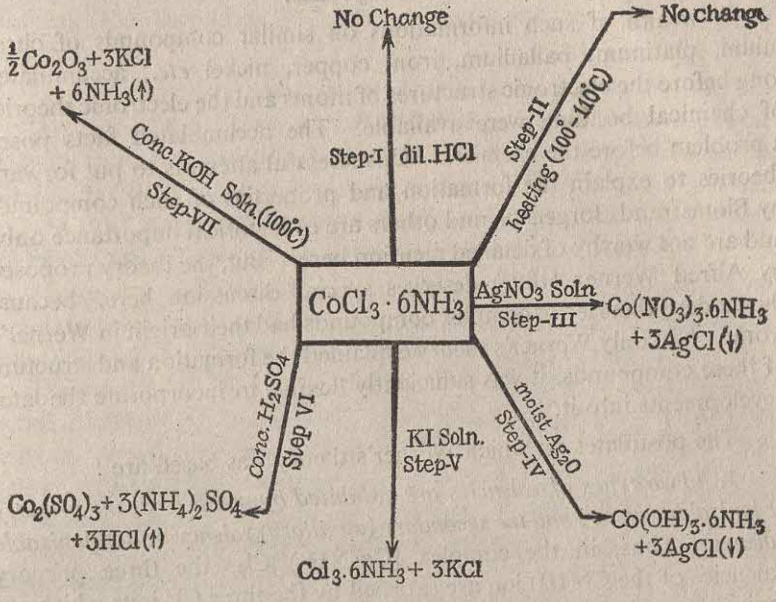


Fig. 7.1

As all the reactions included in the above scheme clearly indicated the presence of a strongly bound complex unit, $[Co(NH_3)_6]^{+3}$, the luteo cobaltic chloride molecule was represented by the structural formula $[Co(NH_3)_6]Cl_3$, which can ionise as :

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{+3}+3Cl^-.$$

This structural formula and ionisation scheme is further confirmed by its molecular conductivity, $\lambda_{1024} = 432$, which is indicative of the presence of four ions in solution.

Following similar lines of arguments, the structures of the cobalt (III) complexes mentioned earlier are :

$CoCl_3.5NH_3.H_2O$ : $[Co(NH_3)_5.H_2O]Cl_3$

$CoCl_3.5NH_3$ : $[Co(NH_3)_5.Cl]Cl_2$

*$CoCl_3$ $4NH_3$ : $[Co(NH_3)_4.Cl_2]Cl$

---

*The difference in the internal structure of this molecule, which gives rise to the green and the violet variety, will be discussed later, when we will deal with geometrical isomerism in complex compounds.

### Werner's theory of Coordination Compounds.

A wealth of such informations on similar compounds of chromium, platinum, palladium, iron, copper, nickel *etc.*, accumulated long before the electronic structures of atoms and the electronic theories of chemical bonding were available. The accumulated facts posed a problem before the chemists. Unsuccessful attempts to put forward theories to explain the formation and properties of such compounds by Blomstrand, Jorgenson and others are of historical importance only, and are not worthy of detailed mention here. But, the theory proposed by Alfred Werner (1893) deserves special discussion here, because the modern theories of complex compounds had their origin in Werner's work. Not only Werner's theory explained the formation and structure of these compounds, it was sufficiently flexible to incorporate the later developments into it.

The postulates on which Werner's theory was based are :

1. *Two types of valencies are exhibited by metal ions, the primary or ionizable valency and the secondary (auxiliary) valency or non-ionizable valency.* Thus, in the complex $[Co(NH_3)_6]Cl_3$, the three primary valencies of the Co(III) ion are satisfied by the three $Cl^-$ ions which are ionizable, and the non-ionizable secondary valencies of the $Co^{+3}$ ion are satisfied by the six ammonia molecules. The metal ion and the ligands attached to it by secondary valencies generally make up the *inner* or *first coordination sphere* which is usually enclosed by a square bracket.

2. *Every metal has a fixed* number of secondary valencies or coordination number.* Thus, the coordination number of Co(III) in $[Co(NH_3)_6]Cl_3$ is six. Ions like Co(III), Cr(III), Fe(III), Pt(IV) *etc.* possess a coordination number six, whereas the coordination number of Ag(I) is 2, that of Cu(II) in $[Cu(NH_3)_4]SO_4$ is 4 and that of Pd(II) is also 4.

3. *The primary or ionizable valencies of a metal are satisfied by anions, but the secondary valencies can be satisfied by anions, neutral molecules and even by positive charge-bearing species like the* $NO^+$ *entity.* In many cases, the negative ion satisfies both the primary and the secondary valencies, as is done by the cyanide ion in the ferrocyanide ion $[Fe(CN)_6]^{4-}$ or the ferricyanide ion $[Fe(CN)_6]^{3-}$. The example of

---

*The coordination number of a metal ion is not always fixed. $Ni^{+2}$ and $Cu^{+2}$ exhibit coordination numbers of both 4 and 6. This is true for several other metal ions, and in the case of a particular metal, it can vary with the oxidation state of the metal. Thus, Pt(II) has a coordination number of four, but P(IV) is six-coordinated.

the anions satisfying the primary valencies, and the neutral molecules satisfying the secondary valencies of a metal ion, is found in $[Co(NH_3)_6]Cl_3$.

4. *The secondary valencies of a metal are directed in definite directions in space. Thus, metals exhibiting a coordination number six have their six valencies directed to the corners of an octahedron, with the metal ion at its centre.* A four coordinated metal ion can have its four secondary valencies directed either to the four corners of a square-plane or to the corners of a tetrahedron.

The existence of a variety of different types of isomerisms originates from this postulate and the proof of their occurrence, furnished by Werner himself, established Werner's theory on a firm footing.

It should be mentioned here that, for a particular metal ion, the overall charge on the complex is entirely dependent on the nature of the ligand associated with the metal ion. Thus, the total charge on the complex entity changes with the number of negatively charged ligands entering into the coordination zone. The gradual change in the charge of a complex ion with the gradual entry of negative ions into the first coordination sphere is shown below :

$$[Co(NH_3)_3]^{+3}Cl_2\ ;\quad [Co(NH_3)_5Cl]^{+2}Cl_2\ ;\quad [Co(NH_3)_4Cl_2]^{+}Cl$$
$$[Co(NH_3)_3Cl_3]^{0}.$$

**Coordination number and stereochemistry.**

In the postulates of Werner's theory, we have noted that, the complexes with a coordination number six (hexa-coordinated complexes) have *octahedral* stereochemistry, while tetra-coordinated complexes possess either *tetrahedral* or *square-planar* stereochemistry. Though 4 and 6 are the most common and widely occurring coordination numbers, metal ions having coordination numbers 2, 3, 5, 7 and even greater than seven are also known. However, we will focuss our attention mainly on the complexes in which coordination numbers 4 and 6 are exhibited by the metal ions. In assigning definite stereochemistries to complexes of different co-ordination numbers, we must keep in mind the principles of the VSEPR theory (discussed in the chapter on chemical bonding). We must remember that, (*a*) *the ligands must be arranged around the metal ion in a manner which minimises the repulsion between them and* (*b*) *the coordination number of a metal ion tends to assume the largest possible value, since, an attraction between it and the dipolar or anionic ligand is responsible for the complex formation, and a close-packed structure will impart maximum stability to the system.*

In our discussion on the VSEPR theory, which is corroborated by the principle of hybridisation of orbitals, we have discussed the most stable configurations of the molecules of the type $AX_2$ (coordination number, C.N. = 2), $AX_3$ (C.N. = 3), $AX_4$ (C.N. = 4), $AX_5$ (C.N. = 5) and $AX_6$ (C.N. = 6). The same line of arguments is applicable to the stereochemistries of the coordination complexes. The following table (Table 7.4) contains some examples of complexes of different coordination numbers, their stereochemistries and the hybrid orbitals responsible for the stereochemistries.

TABLE 7.4

| Coordination number (C.N.) | Examples | Stereochemistry | Orbital Hybridisation involved |
|---|---|---|---|
| 2 | $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$<br>$[Hg(CN)_2]^-$, $[AuCl_2]^-$ | linear | *sp* |
| 3 | $[HgI_3]^-$<br>$[Ag(R_3P)_3]^+$<br>($R_3P$=Triarylphosphine.) | distorted equilateral triangle | $sp^2$ |
| 4 | $[CoCl_4]^{2-}$, $Ni(CO)_4$ | tetrahedral | $sp^3$ |
| 4 | $[Pt(NH_3)_2Cl_2]$, $K_2[PdCl_4]$,<br>$[Cu(gly)_2]$, $[Ni(CN)_4]^{2-}$<br>(glyH=glycine) | square planar | $dsp^2$ |
| 5 | $Fe(CO)_5$, $MoCl_5$ | trigonal bipyramid | $dsp^3$ |
| 5 | $[SbF_5]^{2-}$, $[VO(acac)_2]$,<br>$[Ni(DMG)_2Br]$<br>(DMGH=dimethyl glyoxime | square pyramid | $sp^3d$, $dsp^3$ |
| 6 | $[Co(NH_3)_6]Cl_3$,<br>$K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$,<br>$Na_3[FeF_6[$. | octahedral | $d^2sp^3$<br>$sp^3d^2$ |

**Electronic interpretation of complex compounds.**

Werner's theory was propounded at a time when the electronic structures of atoms and molecules were not known. But, as time marched on, the necessity of putting it on an electronic basis was acutely felt, and Sidgwick and Lowry came forward with their *theory of coordinate or semipolar bonding*, in which the coordinate bond is formed between the two combining entities, one of which *donated* the *electron-pair* responsible for the new chemical bond, while the other *accepted* it. Sidgwick pointed out that all the molecules or ions acting as ligands had at least one unshared pair or *lone* pair of electrons in their valence-shell. According to him, the ligand donates one of its lone-pairs to the metal ion and this gives rise to the secondary valency conceived by Werner. Thus, the formation of a coordinate bond in a metal complex is due to a donor-acceptor interaction between the ligand and the metal, and is comparable to the acid-base or neutralisation process in the *Lewis sense.* We have already discussed about the coordinate bond in the chapter on chemical bonding and we know that, a coordinate bond is, in reality, *a type of covalent bond, differing only in the mode of formation, but similar in every other respect with a normal electron-pair covalent bond.*

Originally, Sidgwick used an arrow to indicate the transfer of an electron-pair to the metal ion, but many authors prefer a solid line, although both the usages are still in vogue. Thus, the structural formulas for the ions $[Co(NH_3)_6]^{+3}$, $[CO(NH_3)_5Cl]^{+2}$ and $[Co(NH_3)_4Cl_2]^{+1}$ and the species $[Co(NH_3)_3Cl_3]^0$ are represented as in fig. 7.1, each arrow represents a coordinate covalent bond.

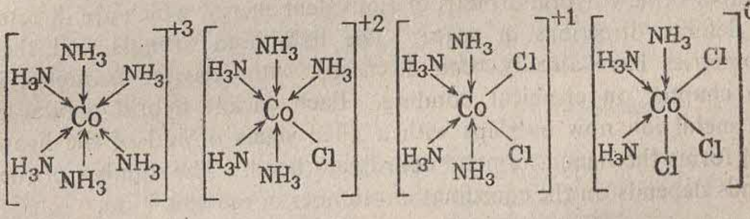


Fig. 7.2

*Defects of Sidgwick's theory* :

Sidgwick's electronic theory suffers from the defects that (a) the donation of six electron-pairs from the six ammonia molecules to the Co(III) ion should result in the accumulation of excessive negative charge on it, which is a very unnatural situation and energetically highly unstable, and (b) the lone-pairs of electrons that are donated to the cobalt (III) ion,are paired up *s*-electrons which have no directional characteristics. But, we know that the bonds between the ligands and the metal are strong covalent bonds with definite, directional characteristics.

**Pauling's theory of hybridisation of orbitals : the valence bond theory.**

The valence bond theory of Pauling, invoking the hybridisation of orbitals, takes care of the above defects and explains the formation and structure of complexes in a logical fashion. Since the energies of the $(n-1)d$, $ns$ and $np$-orbitals differ very little in the transition metal ions, a rearrangement of electrons among these orbitals can occur, resulting in the formation of **hybrid orbitals,** possessing definite directional characteristics. We have already discussed the formation and characteristics of hydrid bond-orbitals in the chapter on chemical bonding.

According to the valence bond theory, the formation of a complex by the interaction of a metal ion and the ligands, involves the following steps :

Prior to the formation of a complex, the metal ion undergoes electron rearrangement, if necessary, and makes available the requisite number of empty orbitals to accommodate the electron-pairs to be donated by the ligands, leading to the formation of coordinate bonds. The number of such vacant orbitals on the metal ion receiving electron-pairs from ligands represents its coordination number.

The vacant metal-orbitals undergo hybridisation to give an equal number of new hybrid orbitals of equivalent energy, which are directed in definite directions in space. The hybridised orbitals and their geometries have already been discussed, with relevant examples, in the chapter on chemical bonding. Each vacant hybrid orbital of the metal ion now overlaps with a filled **sigma** orbital of the ligand and forms the ligand-to-metal coordinate bond. The number of such bonds depends on the coordination number of the metal ion.

The *d*-orbitals involved in hybridisation may be the inner $(n-1)d$ orbitals or the outer *nd*-orbitals, since the energies of the $(n-1)d$, $ns$ and $np$-orbitals, as a group, and the energies of the $ns$-, $np$- and $(n-1)d$-orbitals differ very little among themselves in the transition elements. The complexes formed by the involvement of the $(n-1)d$-orbitals are known as the **inner orbital complexes** or **low-spin complexes,** while those in which the *nd*- orbitals participate, are called the **outer orbital** or **high-spin** complexes.

The non-bonding electrons of the metal ion occupy the unhybridised inner *d*-, *p*- or *s*-orbitals. The re-organisation of these non-bonding electrons obeys Hund's rule of maximum multiplicity, and strives to have the maximum number of unpaired electrons.

We will now consider a few coordination complexes and illustrate the above points. In the discussion that follows, the orbitals are designated by square boxes and the electrons are denoted by arrows. As we have already discussed the principles of hybridisation of orbitals in considerable details in the chapter on chemical bonding, here we shall be as brief as possible. Since, 2, 3 and 5 coordination numbers are of rare occurrence and hence, are of less importance, we will focuss our attention only on the 4-coordinated and 6-coordinated complexes.

**Stereochemistry of 4-coordinated complexes.**

We have already noted that a four coordinated complex, $MA_4$, can assume either tetrahedral or square-planar configuration. Since Ni(II) forms both square-planar and tetrahedral complexes, we will consider the relevant complexes of Ni(II). The rearrangement of the electrons in Ni(II), prior to its acceptance of four lone pairs from four ammonia molecules, leading to the formation of the tetrahedral $[Ni(NH_3)_4]^{+2}$ ion, may be represented diagramatically as follows :

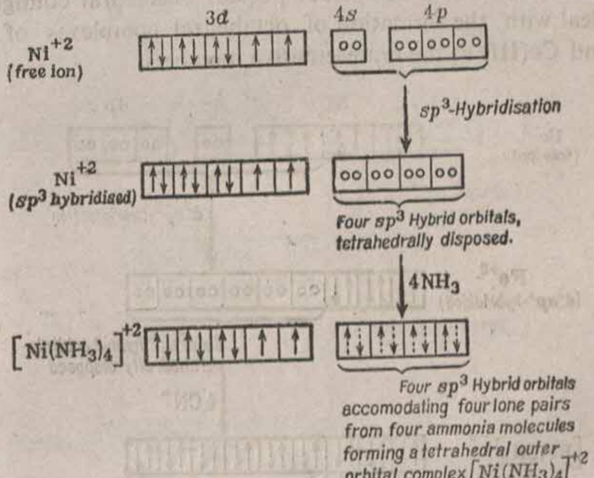

3d
4s
4p
Ni+2 (free ion)
sp3-Hybridisation
Ni+2 (sp3 hybridised)
Four sp3 Hybrid orbitals, tetrahedrally disposed.
4NH3
[Ni(NH3)4]+2
Four sp3 Hybrid orbitals accomodating four lone pairs from four ammonia molecules forming a tetrahedral outer orbital complex [Ni(NH3)4]+2

Fig. 7.3

The formation of the square planar complex $[Ni(CN)_4]^{2-}$ can be pictured as :

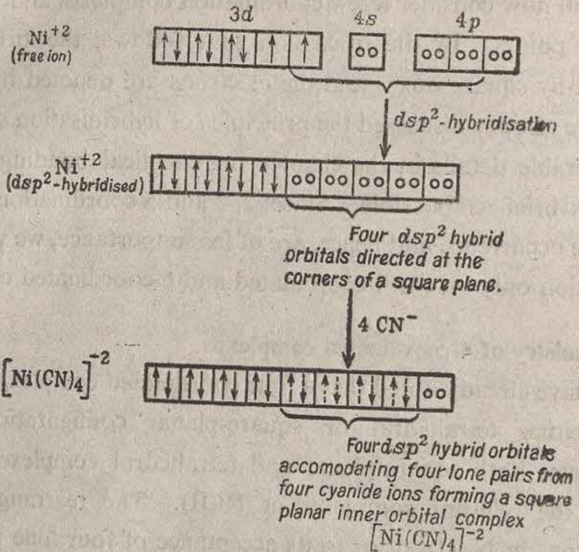

3d
4s
4p
Ni+2 (free ion)
dsp²-hybridisation
Ni+2 (dsp²-hybridised)
Four dsp² hybrid orbitals directed at the corners of a square plane.
4 CN⁻
[Ni(CN)4]-2
Four dsp² hybrid orbitals accomodating four lone pairs from four cyanide ions forming a square planar inner orbital complex [Ni(CN)4]-2

Fig. 7.4

### Stereochemistry of 6-coordinated complexes.

Since 6-coordinated complexes possess octahedral configuration, we will deal with the formation of octahedral complexes of Fe(II), Fe(III) and Co(III) as the representative members.

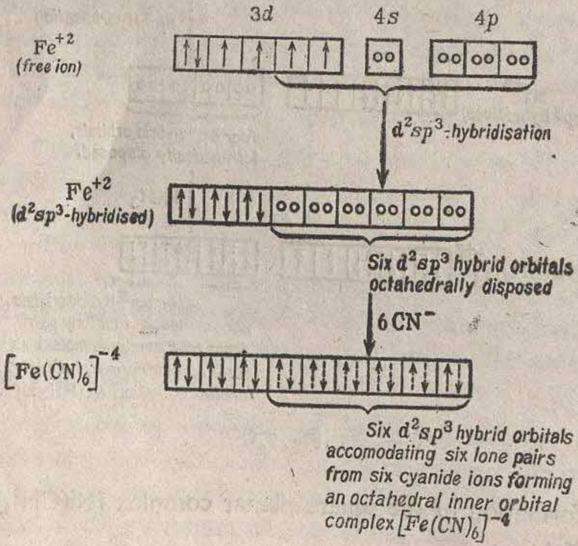

3d
4s
4p
Fe+2 (free ion)
d²sp³-hybridisation
Fe+2 (d²sp³-hybridised)
Six d²sp³ hybrid orbitals octahedrally disposed
6 CN⁻
[Fe(CN)6]-4
Six d²sp³ hybrid orbitals accomodating six lone pairs from six cyanide ions forming an octahedral inner orbital complex [Fe(CN)6]-4

Fig. 7.5

Formation of the inner-orbital complex, $[Fe(CN)_6]^{3-}$, of Fe(III) takes place similarly. However, the formation of the Fe(III) complex, $[FeF_6]^{3-}$, takes place in a different manner :

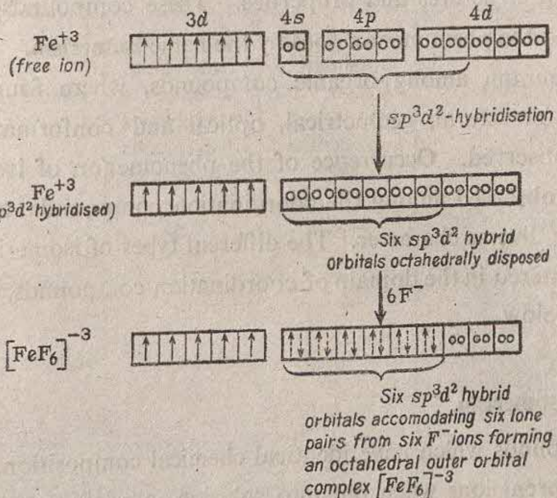

3d
4s
4p
4d
Fe+3 (free ion)
sp3d2-hybridisation
Fe+3 (sp3d2 hybridised)
Six sp3d2 hybrid orbitals octahedrally disposed
6F−
[FeF6]−3
Six sp3d2 hybrid orbitals accomodating six lone pairs from six F− ions forming an octahedral outer orbital complex [FeF6]−3

Fig. 7.6

Formation of $[Co(NH_3)_6]^{+3}$ may be represented as :

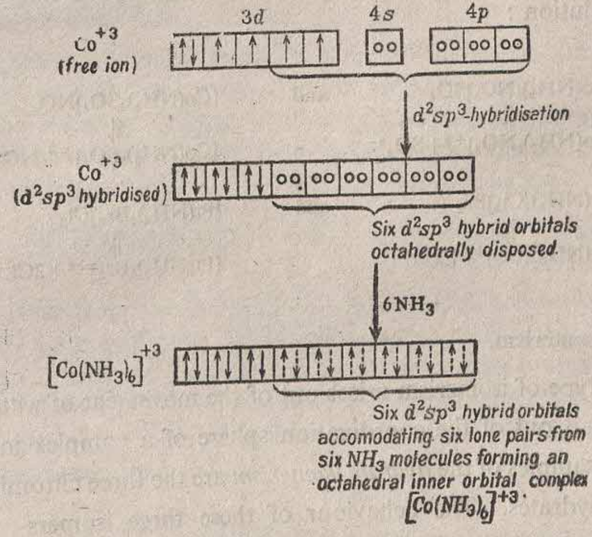

3d
4s
4p
Co+3 (free ion)
d2sp3-hybridisation
Co+3 (d2sp3 hybridised)
Six d2sp3 hybrid orbitals octahedrally disposed
6NH3
[Co(NH3)6]+3
Six d2sp3 hybrid orbitals accomodating six lone pairs from six NH3 molecules forming an octahedral inner orbital complex [Co(NH3)6]+3

Fig. 7.7

## DIFFERENT TYPES OF ISOMERISM ENCOUNTERED AMONG COORDINATION COMPLEXES.

There exist some compounds with identical chemical composition but different structures and properties. These compounds are called **isomers,** and the phenomenon goes by the name **isomerism.** Isomerism is very common among organic compounds, where four types of isomerism (structural, geometrical, optical and conformational) are generally observed. Occurrence of the phenomenon of isomerism is frequently observed among the coordination compounds, and it is of much more diverse character. The different types of isomerism, generally encountered in the domain of coordination compounds, are briefly discussed below.

### Ionisation isomerism.

Compounds which have identical chemical composition, but gives rise to different ions when put into solution, are known as *ionisation isomers.* This happens due to an interchange of anionic or negatively charged ligands inside and outside the coordination zone of a complex. Thus, the following pairs are ionisation isomers, as they yield different ions in solution :

$$\begin{array}{ccc} {[Co(NH_3)_5NO_3]SO_4} & \text{and} & {[Co(NH_3)_5SO_4]NO_3} \\ \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright \\ {[Co(NH_3)_5NO_3]^{+2}+SO_4^{2-}} & & {[Co(NH_3)_5SO_4]^{+}+NO_3^{-}} \end{array}$$

$$\begin{array}{ccc} {[Pt(NH_3)_4Cl_2]Br_2} & \text{and} & {[Pt(NH_3)_4Br_2]Cl_2} \\ \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright \\ {[Pt(NH_3)_4Cl_2]^{+2}+2Br^{-}} & & {[Pt(NH_3)_4Br_2]^{+2}+2Cl^{-}} \end{array}$$

### Hydrate isomerism.

This type of isomerism arises out of the movement of water molecules in and out of the coordination sphere of a complex ion. The classical examples of the *hydrate isomerism* are the three chromium (III) chloride hydrates. The behaviour of these three isomers towards desiccation, towards silver nitrate solution, and the mode of ionisation responsible for such behaviours, are presented in the following table :

TABLE 7.5

| Formula of the isomer | Loss of number of water molecules on keeping over conc. $H_2SO_4$ (desiccation) | Precipitation of number of of $Cl^-$ as AgCl on treatment with silver nitrate. | Mode of ionisation |
|---|---|---|---|
| $[Cr(H_2O)_6]Cl_3$<br>Violet | Zero | Three | $[Cr(H_2O)_6]Cl_3 \rightleftharpoons [Cr(H_2O)_6]^{+3}+3Cl^-$. |
| $[Cr(H_2O)_5Cl]Cl_2.H_2O$<br>Green | One | Two | $[Cr(H_2O)_5Cl]Cl_2.H_2O \rightleftharpoons [Cr(H_2O)_5Cl]^{+2} +2Cl^-+H_2O$. |
| $[Cr(H_2O)_4Cl_2]Cl.2H_2O$<br>Green | Two | One | $[Cr(H_2O)_4Cl_2]Cl.2H_2O \rightleftharpoons [Cr(H_2O)_4Cl_2]^+ +Cl^-+2H_2O$. |

From the formula of the isomers and their mode of ionisation, it can be easily noted that, these examples of hydration isomerism can also be considered as special cases of ionisation isomerism (described before).

**Polymerisation isomerism.**

Complex compounds, having the same stoichiometric composition, but possessing molecular weights which are integral multiples of the simplest stoichiometric arrangement, are called polymerisation isomers, and the phenomenon goes by the name *polymerisation isomerism*. The most common examples of polymerisation isomers are :

$$\underset{\text{I}}{[Pt(NH_3)_2Cl_2]},\ \underset{\text{II}}{[Pt(NH_3)_4]\,[PtCl_4]} \text{ and } \underset{\text{III}}{[Pt(NH_3)_3Cl]\,[Pt(NH_3)Cl_3]}$$

It is clear from the formulas of I and II that, these two are not '*polymers*' in the real sense of the term, which means the repetition of the same structural unit leading to the formation a compound of high molecular weight.* In this case, we have multiplication of molecular weight along with differences in arrangements of the ligand around the metal ions.

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*These are also not true isomers because of different molecular weights.

### Coordination isomerism.

When a complex salt is made up of a complex cation containing one metal, and a complex anion of the same or another metal, a redistribution of all or some of the ligands between the complex cation and the complex anion gives rise to *coordination isomerism.* Some examples of coordination isomerism are :

$[Co(NH_3)_6]\,[Cr(CN)_6]$ and $[Cr(NH_3)_6]\,[Co(CN)_6]$
$[Cr(NH_3)_6]\,[Co(C_2O_4)_3]$ and $[Co(NH_3)_6]\,[Cr(C_2O_4)_3]$
$[Cu(NH_3)_4]\,[PtCl_4]$ and $[Pt(NH_3)_4]\,[CuCl_4]$
$[Cr(NH_3)_6]\,[Cr(CNS)_6]$ and $[Cr(NH_3)_4(CNS)_2]\,[Cr(NH_3)_2(CNS)_4]$

Though previously discussed under polymerisation isomerism, the isomers II and III in page 293 are actually coordination isomers of each other.

### Linkage isomerism or salt isomerism.

Some monodentate ligands possess two different donor atoms. Such ligands are called **ambidentate** ligands. Thus, the $CNS^-$ group can coordinate either through the nitrogen atom or the sulphur atom, and the $NO_2^-$ moiety can form linkage via the nitrogen or the oxygen atom. Examples of some other common ambidentate ligands are, $CN^-$ and $S_2O_3^{2-}$ ions. Linkage isomerism originates when an ambidentate ligand attaches itself to the same metal ion in two different modes, e.g.

| | | |
|---|---|---|
| $[Co(NH_3)_5NO_2]Cl$ | and | $[Co(NH_3)_5ONO]Cl$ |
| yellow | | red |
| *nitro*pentammine | | *nitrito*pentammine |
| (coordination of the $NO_2^-$ group through nitrogen) | | (coordination of the $NO_2^-$ group through oxygen) |

This type of isomerism was earlier called **salt isomerism,** which has now been replaced by the more appropriate term *linkage isomerism.*

### Ligand isomerism.

Complexes of two isomeric ligands necessarily exist as isomers of each other. Thus, copper(II) complexes of α-alanine (α-amino propionic acid) and β-alanine (β-amino propionic acid) are isomeric with each other, *i.e.* the two isomers are : $[Cu(\alpha\text{-}ala)_2]^\circ$ and $[Cu(\beta\text{-}ala)_2]^\circ$ ; (alaH)=alanine.

**Stereoisomerism.**

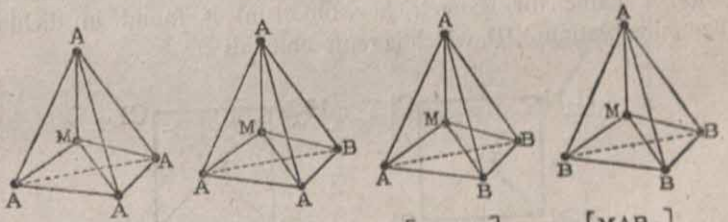
In stereoisomerism, two substances with identical composition of the first coordination sphere, differ only in the relative positions of the different ligands in space around the central metal ion. This is one of the varieties of isomerism predicted by Werner's theory and occurs most widely. Since two such isomers may possess the same geometrical figure, but differ only in the relative arrangements of the ligands in space, it is also known as *geometrical isomerism.*

**Geometrical isomerism.**

Since tetrahedral, planar and octahedral stereochemistries are the most abundant and most important among the possible stereochemical forms, we will restrict our discussion to the geometrical isomerism of each of these forms.

**TETRAHEDRAL STRUCTURE.**

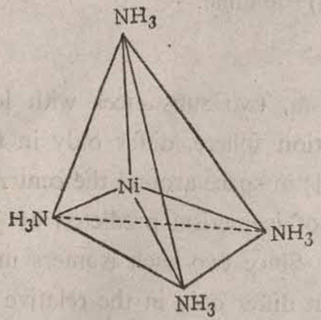
In the tetrahedral structure, each ligand is equidistant from each other and from the central metal ion at its centre, and all the bond angles are 109°28′. Thus, the relative positions of the ligands are always identical in it and hence, geometrical isomerism is not possible among the four-coordinated tetrahedral complexes of the types, $MA_4$, $MA_3B$, $MA_2B_2$ and $MAB_3$, A and B being monodentate ligands.



$[MA_4]$ $[MA_3B]$ $[MA_2B_2]$ $[MAB_3]$

Fig. 7.8

Tetrammine nickel (II) ion, $[Ni(NH_3)_4]^{+2}$ is a familiar example of a tetrahedral complex :

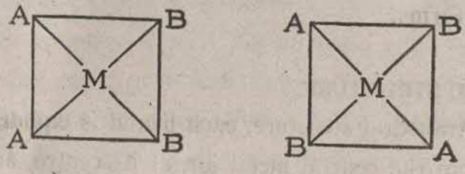


[ Tetrahedral $[Ni(NH_3)_4]^{+2}$ ion )

Fig. 7.9

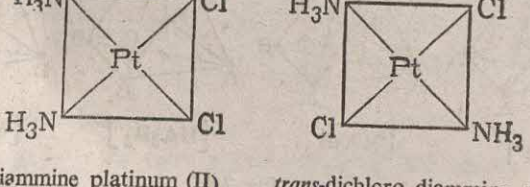
**Square-planar structure.**

In the square-planar structure, complexes of the types $MA_4$ or $MA_3B$ do not give rise to geometrical isomerism. But, complexes of the type $MA_2B_2$ give two geometrical isomers, I and II :



(I) Fig. 7.10 (II)

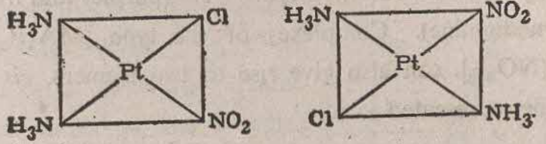
In I, the two identical groups occupy adjacent positions and are in nearest possible positions with respect to each other and is called the *cis*-isomer. In II, the two identical groups are farthest from each other, *i.e.* they are situated opposite to each other, and this is known as the *trans*-isomer. A typical example of *cis-trans isomerism* (another name for geometrical isomerism) is found in dichloro-diammine platinum(II), which is represented as



*cis*-dichloro diammine platinum (II) *trans*-dichloro diammine platinum (II)

Fig. 7.11

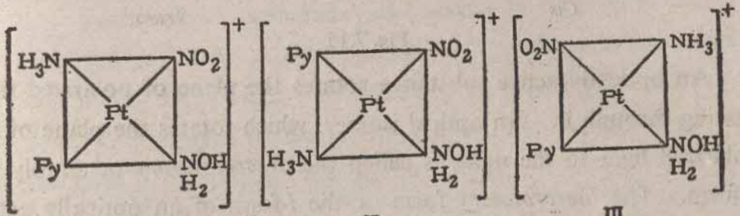
Two geometrical isomers of the complexes of the type $MA_2BC$ are also known, where A, B and C are different ligands.



I (cis) II (trans)

Fig. 7.12

The complexes of the type MABCD, where A, B, C and D are different ligands, are found to exist in three isomeric forms. Three such isomers of the complex $[Pt(NH_3)(NH_2OH)(Py)NO_2]$ are shown below :

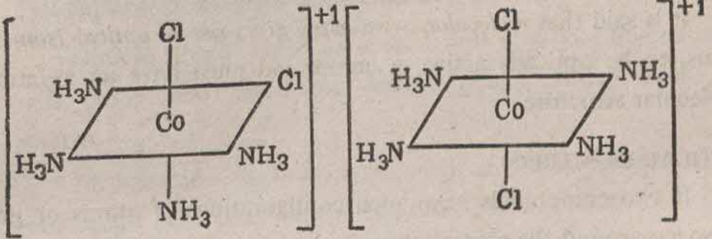


I II III

Fig. 7.13

### Octahedral stereochemistry.

In octahedral stereochemistry, the complexes of the types $MA_6$ and $MA_5B$ do not give rise to geometrical isomers. However, when another A is replaced by B, two geometrical isomers come into existence, one is *cis* and the other is *trans*. Thus, the complex ion $[Co(NH_3)_4Cl_2]^+$ exists as :



I II

Fig. 7.14

I. Violet *cis*-dicbloro tetrammine cobalt (III)
II. Green *trans*-dichloro tetrammine cobalt (III)

Some other examples of $MA_4B_2$ type of complexes, existing as *cis-trans* isomers, are : $[Co(NH_3)_4(NO_2)_2]Cl$ —*cis* (yellow-brown) and *trans* (yellow) ; $[Co(en)_2Cl_2]Cl$ — *cis* (purple) and *trans* (green) (en=ethylenediamine). Complexes of the type $[MA_3B_3]$, such as $[Co(NH_3)_3(NO_3)_3]$, can also give rise to two isomers, *cis* and *trans*, which can be represented as :

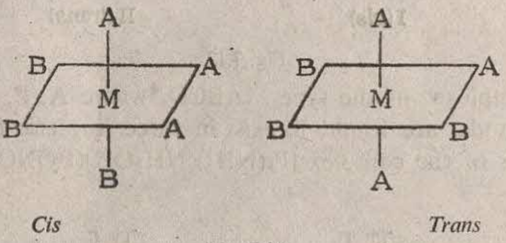


Fig. 7.15

An optically active substance rotates the plane of polarized light passing through it. An optical isomer, which rotates the plane of the polarized light to the right, is called the *dextrorotatory* or simply the *d*-form. The *laevorotatory* form or the *l*-form of an optically active compound is the isomer of the *d*-form, which rotates the plane of polarized light to the left of its original direction. The substance is termed as *inactive*, if the rays of polarized light pass undeviated through it. An equimolecular mixture of the *d*- and the *l*-forms of an optically active compound is called the *racemic* variety. A ray of polarized light, after passing through a racemic variety, shows no resultant deviation from its original direction, as its dextrorotation by the *d*-form is exactly balanced by the laevorotation due to the *laevo*-variety.

It is said that *molecular asymmetry gives rise to optical isomerism.* Thus, to be optically active, a compound must have an asymmetric molecular structure.

## OPTICAL ISOMERISM.

If two compounds have such configurations of atoms or groups in space around the central atom or ion that, one is the mirror-image of the other, they are called *optical isomers* or *enantiomorphs*, and the phenomenon is known as *optical isomerism* or *enantiomorphism*.

We have already noted that, the existence of optical isomerism among octahedral complexes was predicted by Werner's theory. In fact, optical isomers exist in complexes of the $M(A-A)_2B_2$ type, where $A-A$ is a bidentate ligand. The *cis*-isomer of the complex $M(A-A)_2B_2$ can give rise to two distinct mirror-image forms which are not superimposable. Such an example is found in the complex $[Co(en)_2Cl_2]Cl$ which can be represented as in fig. 7.16.

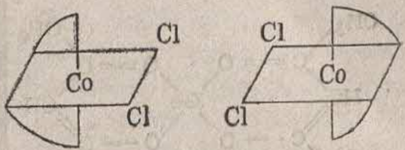


Fig. 7.16
Optical isomers of cis-$[Co\ (en)_2Cl_2]^+$

Such optical isomerism also occurs in octahedral complexes of the type *cis*-$[M(A-A)_2BC]$ and $[M(A\text{-}A)_3]$, where A-A is a symmetrical bidentate donor like the oxalate ion $[(C_2O_4)]^{2-}$, ethylenediamine (*en*), α, α′-dipyridyl (α, α′-dipy) *etc*. The enantiomers of the complex $[Cr\ (C_2O_4)_3]^{3-}$ are represented as :

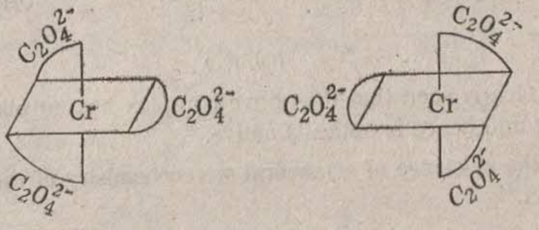


Fig. 7.17

**Optical isomers of metal complexes with coordination number 4.**

Optical isomers of some special type of 4-coordinated complexes with both tetrahedral and square planar configuration are also known.

*Tetrahedral complexes* : In analogy with carbon compounds, tetrahedral complexes of the type MABCD was expected to exhibit optical isomerism. But, this has not been found in practice. However, tetrahedral complexes of Be(II), B(III) and Zn(II) with two unsymmetrical bidentate ligands have been resolved into optically active forms. Such a ligand is benzoyl acetone and the two optical isomers of its Be(II) complex are shown below (fig. 1.18.)

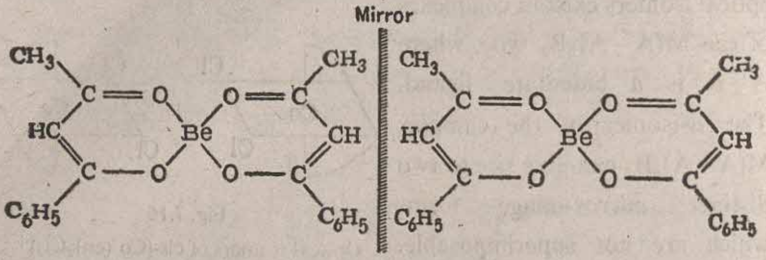


Fig. 1.18

*Square-planar complexes* : One square-planar complex is found to yield optical isomers and is shown below :

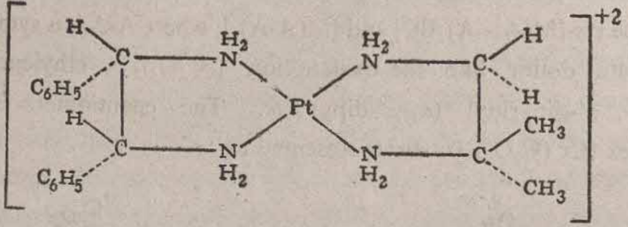
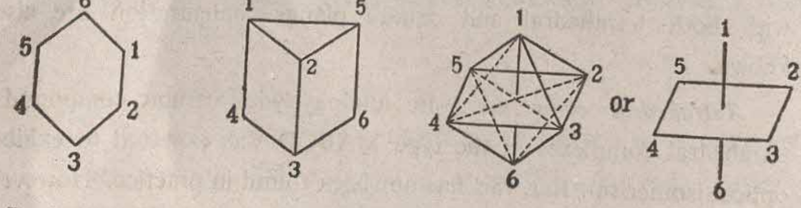


Fig. 1.19

It is clearly seen that the above complex has no plane or axis of symmetry and hence is optically active.

**Proof of the existence of octahedral stereochemistry of the coordination number six.**

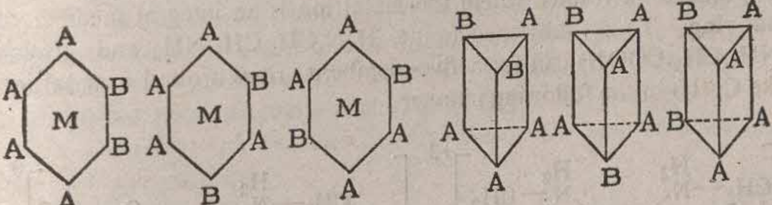
A hexagon, a trigonal prism and an octahedron are the three geometrical figures capable of accommodating six donors, the central metal ion being placed at their centres. In all these figures, all the corners (marked as 1,2,3, to 6) are equidistant from the central metal ion.



*Regular hexagon* *Trigonal prism* *Octahedron*

Fig. 7.20

That the octahedral stereochemistry is the arrangement preferred by the hexa-coordinated complexes, is established through an extensive studies of the geometrical and optical isomers of the hexa-coordinated complexes. In practice, the number of geometrical isomers, predicted for a particular complex by each configuration, is counted first. Then these numbers are compared with the number of isomers actually isolated experimentally. That particular geometrical arrangement is taken to be the correct one, which predicts the actual number of isomers that have been obtained experimentally. Thus, in the case of $MA_6$ and $MA_5B$-type of complexes, only one form is predicted by each of the three geometries. For $MA_4B_2$-type complexes, the hexagonal and prismatic geometries predict the existence of three isomers (fig. 7.21) :



*1:2 or Ortho isomer* *1:3 or Meta isomer* *1:4 or Para isomer* *1:2 Isomer* *1:3 Isomer* *1:4 Isomer*

Fig. 7.21

while the octahedron predicts only two isomers (fig. 7.22) :

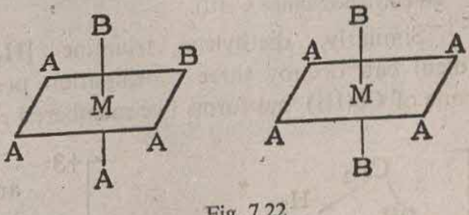


Fig. 7.22

In practice, for complexes like $[Co(NH_3)_4Cl_2]^+$, only two isomers, whose structures were already shown in Fig. 7.14, have been isolated. In the case of $[MA_3B_3]$-type of complexes like $[Cr(H_2O)_3Cl_3]$, three isomers are predicted by both the hexagonal (1, 2, 3 ; 1, 2, 4 ; 1, 3, 5) and the prismatic (1, 2, 3 ; 1, 2, 5 ; 1, 2, 6) configurations. But, the octahedral configuration predicts only two isomers (1, 2, 3 and 1, 2, 6). In practice, not more than two isomers of $[Cr(H_2O)_3Cl_3]$ have ever been isolated. Hence, the octahedral configuration is the correct one for hexa-coordinated complexes.

The final proof of the octahedral configuration came from the correct prediction of the existence and the number of optical isomers in some hexa-coordinated complexes. Thus, both the hexagonal and the prismatic forms do not predict the existence of optical isomers in the complexes of the type [M(A–A)$_3$], where A–A is a bidentate chelating ligand. But, the octahedron predicts that, two mirror-image forms of the compound must exist. In practice, quite a number of such complexes like [Co(en)$_3$]$^{+3}$, [Co(dipy)$_3$]$^{+3}$ has been resolved into the *d*- and *l*- varieties. Determination of the three-dimensional structures of many hexa-coordinated complexes by X-ray diffraction technique has confirmed their octahedral stereochemistry.

## CHELATES.

When a ligand molecule can simultaneously occupy more than one position within the coordination sphere of a single metal ion, ring formation results, where the metal ion is an integral member of that ring. Thus, ethylenediamine, $H_2N.CH_2.CH_2.NH_2$ and glycine ($NH_2.CH_2.COOH$) can form five-membered rings around a metal ion like Cu(II) in the following manner :

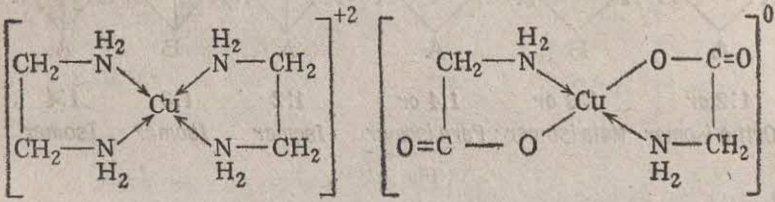


Fig. 7.23

bis-ethylenediamine Cu(II). bis-glycinato Cu(II).

Similarly, diethylene triamine [$H_2N.(CH_2)_2.NH.(CH_2)_2.NH_2$] (dien) can occupy three coordination positions in the coordination zone of Co(III) and forms five membered rings around it :

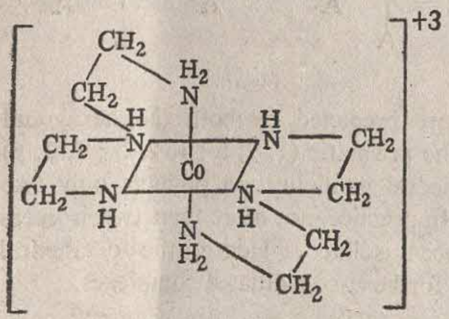
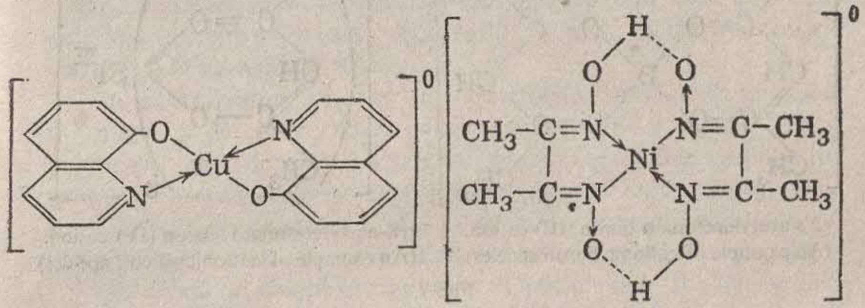


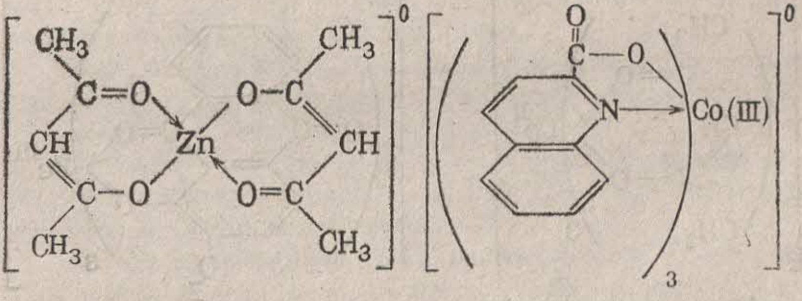
Fig. 7.24
bis- dien cobalt (III).

Such ring-forming ligands are called polydentate ligands. But, they are more familiar by the name **chelating ligands** [the word **chelate** originates from the Greek word "**chele**", meaning **crab's claw** or simply claw. Just as a ring is formed when a crab holds anything with its claws, a ring results when a chelating ligand holds on or coordinates to a metal ion]. The rings, thus formed, are called **chelate rings** and the complexes themselves are knwon as **metal chelates.** Depending on the number of donor sites present in one molecule of a chelating ligand, which it can donate to a single coordination sphere, the chelating ligands are classified into **bidentate, tridentate, tetradentate, pentadentate, hexadentate** *etc.*, according to their capacity of spanning two, three, four, five or six positions in a single coordination sphere. However, in common usage, the chelating ligands, higher than the bidentates, are collectively termed as polydentate ligands. We have seen that the glycine molecule, $H_2N.CH_2.COOH$, possesses a neutral donor group as the $-NH_2$ and a salt-forming or acidic group in the form of the carboxyl group, $-COOH$. Thus, in one stroke, the two glycinate ions can satisfy the coordination number (4) and the oxidation state (+2) of the Cu (II) ion, and forms a chelate [see fig. 7.23], bearing no charge. **Such chelate complexes, in which both the oxidation state and the coordination number are simultaneously satisfied by a chelating ligand, are called inner-metallic complexes or simply inner complexes of the first order.** A few familiar examples of such inner-metallic complexes are given below :



Cu(II) oxinate

Ni(II) dimethylglyoximate



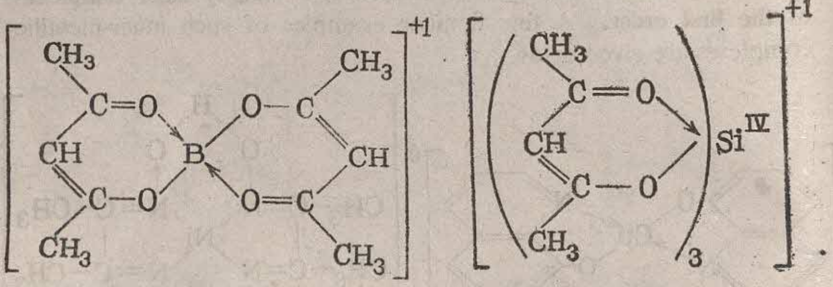
Zn(II) acetylacetonate

Co(II) quinaldinate

Fig. 7.25

Since these complexes are non-electrolytes, many of them can be extracted into organic solvents and hence, are very useful in separating difficultly separable metal ions. Many of them, being quite intensely coloured, are used for both qualitative detection and quantitative estimation of metal ions by colorimetry or spectrophotometry. The insolubility of them in aqueous media has also been used to employ them as reagents for the gravimetrie estimation of metal ions. When, in an inner-metallic complex, the coordination number of the metal ion is fully satisfied, but its oxidation state or positive charge is (a) only partly satisfied or (b) exceeded by the negative charges on the ligand anions within the coordination zone, **inner-metallic complexes of the second order** results. It is quite obvious that cases (a) will lead to cationic inner complexes while (b) will result in the formation of inner complexes of the anionic type. Examples of both types of second order inner complexes are given below :

*Type* (a) *cationic inner complexes*

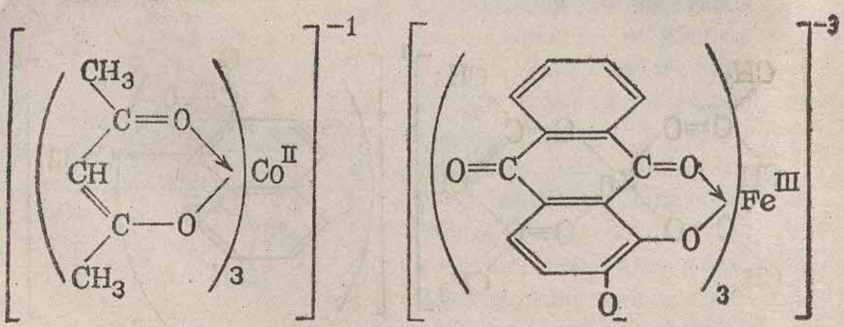


*bis*-acetylacetonato boron (III) cation. (An example of cationic boron species)

tris-acetylacetonato silicon (IV) cation. (An example of cationic silicon species).

Fig. 7.26

*Type* (b) *anionic inner complexes.*



acetylacetone complex of Co (II)

Alizarin complex of Fe (III)

Fig. 7.27

### Applications of complex compounds in different fields.

Many, many years before they were recognised as **complex** compounds, a large number of natural and synthetic complex compounds were used by man in the form of paints, pigments and other colouring matters and as medicines. Thus, the practical applications of coordination complexes have a very long history. The major uses of different types of coordination complexes are discussed here, under a few categories.

**Coordination complexes in industry and in daily life.**—Since many of the industrial products are meant for uses in daily life, the uses of complex compounds in industry and in daily life are discussed together. The dissolution of gold in aqua-regia involves the formation of the complex $H[AuCl_4]$. The purification of platinum by dissolution in aqua-regia, and its subsequent purification by precipitation with excess KCl, involve the formation of the complex **potassium chloroplatinate,** $K_2[PtCl_6]$. Extraction of nickel in the Mond's process depends on the formation of the volatile nickel carbonyl complex $Ni(CO)_4$, through which nickel is separated from the other metals present. Metallic nickel is obtained by subsequent decomposition of $Ni(CO)_4$. The aluminium complex **cryolite,** $Na_3[AlF_6]$, is used in the electrolytic extraction of aluminium metal.

In electroplating industry, the electrolyte (solution from which the metal is deposited) often contains complex compounds. Thus, copper-plating is done from a solution containing cyanide ions and the species undergoing electro-deposition is mainly $K_2[Cu(CN)_3]$. The help of such complexation is also taken in the domain of metallurgy, specially in the cyanide process of the extractions of silver and gold.

Coordination complexes find wide applications in the dyeing and printing industries. In the dyeing industry, most of the bright colours used are coordination complexes of organic dye molecules. The metal ions acting as coordination centres are called **mordants** and the dye-metal ion complexes go by the name of **lakes.**

From time immemorial, copper phthalocyanin, known as **monstral blue,** was being used as pigment. Another complex compound widely used as pigment is prussian blue, $Fe_4[Fe(CN)_6]_3$.

Softening of hard water by the use of hexametaphosphate [calgon, $Na_6(PO_3)_6$] involves the formation of complexes of the metal ions which are responsible for the hardness.

Complex compounds are of vital importance in the living world. Thus, metal-complexes like, haemoglobin, vitamin $B_{12}$, many metallo-proteins, metallo-enzymes *etc*. are essential for the maintenance of the life process. Chlorophyll, the magnesium complex, is absolutely essential for plant life, as without it photosynthesis is not possible. Apart from these, many biologically important organic molecules like enzymes, co-enzymes *etc*., can act only through the mediation of metal ions, with which they form transient complexes, which are the actual active species.

In the mineral world, many minerals occur in nature as coordination complexes.

The application of coordination complexes in analytical chemistry cannot be over-emphasised. Some of the more important applications of complexes in chemical analysis are noted below :

**(A) In qualitative detection of some metal ions.**

In group IIA of the analytical chemistry, Cu(II) is detected as the deep blue tetrammine copper (II) ion, $[Cu(NH_3)_4]^{+2}$. Cu (II) and Cd(II) are separated from each other and detected by utilising the differences in the stabilities of their cyanide complexes. In group III, ferric ion is detected by the formation of the complex prussian blue and also as the red thiocyanato complex. In group IIIB, nickel is detected as red bis-dimethyl glyoximato nickel (II), and cobalt (II) is detected as its deep blue complex, $[Co(CNS)_4]^{-2}$.

**(B) In quantitative analysis.**

(i) In gravimetric determination of metals, Ni(II) is completely precipitated as the red coloured first order inner-metallic complex, $[Ni(DMG)_2]$, ( where HDMG=dimethyl glyoxime ), which is insoluble in water in neutral or slightly alkaline medium. This $[Ni(DGM)_2]$ precipitate is dried at 110° – 120°C and weighed. From the weight of this precipitate, the amount of Ni(II) present is calculated. In this manner, Al(III), Mg(II) *etc*. are determined through their water-insoluble complexes with 8-hydroxyquinoline or oxine.

**(ii) Preferential solvent extraction of a metal complex in presence of other metals and spectrophotometric determination of trace quantities.**

Both Fe(III) and Al(III) form inner-metallic complexes with oxine, but while $[Fe(oxin)_3]$ is formed even in acid solution (*p*H 2 – 3), $[Al(oxin)_3]$ is precipitated only above *p*H 7, and the $[Fe\ (oxin)_3]$ complex is soluble in chloroform. Hence, from a solution containing both Fe(III) and Al(III), the complex $[Fe(oxin)_3]$ (formed by the addition of a slight excess of the reagent at *p*H 2 – 3) is extracted out repeatedly with chloroform and made up to a definite volume in a volumetric flask. The amount of iron present can be found out colorimetrically or spectrophotometrically by measuring its optical density at 470 nm, and comparing the value obtained with the optical density of a standard Fe(III) sample.

The above method can also be used for the spectrophotometric determination of *very small or trace quantity* of Fe(III). This is possible because of the high absorption of the inner-metallic complex formed.

(iii) **Removal of interferences in chemical analysis.**

In most cases, when several metal ions are present in the same solution, the organic reagent used forms complexes with other metal ions along with the metal ion which is being determined. Thus, some of the metal ions intefere with the determination of the required metal ion. In such cases, another organic ligand (sometimes inorganic ligands like $CN^-$ are also used) is added prior to the addition of the actual reagent, and this forms very strong soluble complexes with the interfering metal ions and hence makes correct estimation of the desired metal possible. Such reagents are called *masking agents* or *sequestering agents*. Tartaric acid is used as a masking agent to remove the interference of Fe(III) and Cr(III) in the estimation of nickel as $Ni(DMG)_2$ in alloy steels like stainless steel. Ethylenediamine tetraacetic acid (EDTA) is a very efficient and versatile masking agent. Other common masking agents are citric acid, sulphosalicylic acid *etc.*

## COMPLEXOMETRIC TITRATIONS.

EDTA forms *very stable* 1 : 1 complexes with most of the metal ions under varying conditions of *p*H. This property of EDTA has been used for the complexometric determination of a large number of metal ions. There are many metal-sensitive indicators, which are coloured organic ligand molecules that change their colour on complexation with the metal ions. Thus, Eriochrome black T is coloured blue in alkaline solution ($p$H$=10$), but becomes purple in presence of $Ca^{+2}$ and $Mg^{+2}$. Hence, when a purple solution containing Eirochrome black T and $Ca^{+2}$ and $Mg^{+2}$ ($p$H$=10$), is titrated with a standard EDTA solution, the $Ca^{+2}$ and $Mg^{+2}$ ions are gradually converted into their very stable EDTA complexes. At the end point, when the last traces of $Ca^{+2}$ and $Mg^{+2}$ are complexed by the last drop of the EDTA solution, the Eriochrome black T will assume its own free colour, *i.e.*, at the end-point, the colour will change from purple to blue. This is an example of competitive complex-formation of two ligands being utilised for practical purposes.

CHAPTER VIII

# RARE GASES

## [ *The Inert Gases or the Noble Gases* ]

### ELEMENTS OF GROUP ZERO

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The six gases, helium, neon, argon, krypton, xenon and radon are known as the *rare gases*. The first five of them are present in the atmosphere in very small quantities and the last one results from the disintegration of certain radioactive materials such as radium.

The atmospheric content of these gases are given below :

| Gas | Volume % | Weight % |
|---|---|---|
| Helium | $5 \times 10^{-4}$ | $7 \times 10^{-5}$ |
| Neon | $1.8 \times 10^{-4}$ | $1.2 \times 10^{-4}$ |
| Argon | $9.34 \times 10^{-1}$ | 1.286 |
| Krypton | $1.1 \times 10^{-4}$ | $3 \times 10^{-4}$ |
| Xenon | $9 \times 10^{-6}$ | $4 \times 10^{-5}$ |

The natural occurrence of radon is estimated as $5 \times 10^{-18}\%$ by volume and $4 \times 10^{-17}\%$ by weight. The name *rare gases* has been given to them for their availability in such minute amounts. They are also called the *inert gases* or the *noble gases* due to their general chemical inertness, although some of their compounds have been prepared recently under special conditions.

The electronic structure of their atoms have valence shells which are closed octets (a duplet in the case of He). Such a stable electronic configuration of the atoms, with fully paired maximum number of electrons that the outermost shell can accommodate, results in their high ionization potentials and negligible electron affinities. Thus, the atoms of the rare gases have no tendency either to gain or lose electrons and hence, they are incapable of forming electrovalent or covalent compounds. This accounts for the chemical inertness of the rare gases and this is also the reason why two atoms of such gases cannot combine together to form diatomic molecules. They are, therefore, considered as zero-valent elements. The electronic structures of the atoms of the rare gases are given below :

| Element | At. No. | 1*s* | 2*s* | 2*p* | 3*s* | 3*p* | 3*d* | 4*s* | 4*p* | 4*d* | 4*f* | 5*s* | 5*p* | 5*d* | 6*s* | 6*p* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| He | 2 | 2 | | | | | | | | | | | | | | |
| Ne | 10 | 2 | 2 | 6 | | | | | | | | | | | | |
| Ar | 18 | 2 | 2 | 6 | 2 | 6 | | | | | | | | | | |
| Kr | 36 | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | | | | | | | |
| Xe | 54 | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | | 2 | 6 | | | |
| Rn | 86 | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 14 | 2 | 6 | 10 | 2 | 6 |

The numerical values of some of the physical properties of these gases are summarised below, from which it will be seen that nearly linear relationship are apparent between variations in many of these properties and variations in atomic number or weight.

TABLE 8.1

| Property | He | Ne | Ar | Kr | Xe | Rn |
|---|---|---|---|---|---|---|
| Atomic number | 2 | 10 | 18 | 36 | 54 | 86 |
| Atomic weight | 4 | 20.19 | 39.94 | 83.8 | 131.3 | 222 |
| Atomic radius (Å) | — | 1.60 | 1.91 | 2.0 | 2.2 | — |
| Density (g/ml. liq.) | 0.126 | 1.204 | 1.65(s) | 2.6 | 3.06 | 4.4 |
| Atomic volume (ml. Liq.) | 31.77 | 16.76 | 24.21(s) | 32.19 | 42.92 | 50.46 |
| Melting pt. (°K) | 0.9(?) | 24.43 | 83.9 | 104 | 133 | 202 |
| Boiling pt. (°K) | 4.216 | 27.2 | 87.4 | 121.3 | 163.9 | 211.3 |
| 1st ionization potential (ev) | 24.58 | 21.56 | 15.76 | 14 | 12.13 | 10.75 |
| Solubility in water (ml./lit.) at 20°C. | 13.8 | 14.7 | 37.9 | 73 | 110.9 | — |

**Position of the Rare gases in the Periodic Table.**

The most abrupt change in the electrical character of the elements from the most electronegative halogens in the Group VII of the Periodic Table to the most electropositive alkali metals in Group I, appeared very puzzling to the chemists in corroborating the principle of smooth transition or change in the properties of elements from one group to the next, as envisaged in the periodic classification. Thomson suggested that there should be a group of elements in between the most electronegative halogens ($ns^2p^5$) and the most electropositive alkali metals [$(n+1)s^1$], and such elements should possess almost neutral electrical properties ($ns^2p^6$). Mendeleyev's Periodic Table did not contain such elements, as these were not known when the Table was compiled. With the discovery of argon and helium, the idea of Thomson appeared to be true, as these two elements were found to be inert and were thought to have *zero valency*. So, helium (atomic weight, 4) was placed before lithium (at. wt., 7), and argon (at. wt., 39.94) before potassium (at. wt. 39.01), in the same vertical column with helium (due to its analogy with helium), although the atomic weight demanded a reversed placement. The subsequent discovery of neon, krypton, xenon and radon nicely fitted in the same group with helium and argon. All these gases were found to be chemically inactive, indicating the absence of all chemical affinity or valency, and they formed a complete and separate group (as suggested by Ramsay), placed before Group I of the strongly electropositive alkali metals and after the Group VII of the strongly electronegative halogens. This is justified by the argument that an abrupt change from a highly electronegative to a highly electropositive character, or *vice-versa*, in elements can occur only through a zero stage of character.

| Electronegative elements of Gr. VII | Elements of Gr. O | Electropositive elements of Gr. I |
|---|---|---|
| .... | He (2) | Li (3) |
| F (9) | Ne (10) | Na (11) |
| Cl (17) | Ar (18) | K (19) |
| Br (35) | Kr (36) | Rb (37) |
| I (53) | Xe (54) | Cs (55) |

**Occurrence.**

The main source of the rare gases is the atmosphere where they occur to the extent of about 1 volume-per cent. Argon is the principal constituent thereof, with the other gases present only in quite small quantities, as stated earlier. Helium occurs in many natural gas-wells in the United States and Canada. Gases rich in argon, and especially in helium, are given off by many mineral water (as in Bakreswar in West Bengal, India). Neon has occassionally also been found therein. Helium is found occluded in many radioactive minerals like *pitchblende*, *cleveite*, *monazite etc.*, where it is formed by the radioactive transformations in which α-particles are emitted. Small amounts of radon (and other radioactive emanations, *viz.* thoron and actinon, which are isotopic with radon) are produced in the radioactive decay of radium (or thorium and actinium).

## The History of the Discovery of the Rare gases.

The inert gases were discovered and identified entirely by physical methods during the course of eighteenth and nineteenth-century studies of the atmosphere. The first indication of their presence was noted by Cavendish (1785), who reported that he was unable to completely eliminate, by chemical means, a small residue, "not more than 1/120 of the whole", from any sample of atmospheric air. His experiment was in fact very precise, but he failed to recognise this residue as a third constituent of atmospheric air, *viz.* argon.

**Cavendish's Experiment.**—Cavendish passed electric spark through a large volume of air mixed with excess of pure oxygen, contained in a big round-bottomed flask, when nitrogen reacted with oxygen, forming oxides of nitrogen. These were absorbed by strong caustic soda solution.

$$N_2+O_2 \xrightarrow{\text{electric spark}} 2NO;$$

$$2NO+O_2 \longrightarrow 2NO_2.$$

$$2\,NO_2+2\,NaOH \longrightarrow NaNO_3+NaNO_2+H_2O.$$

After treating the residual gas, which was supposed to be residual oxygen, with alkaline pyrogallate solution (absorbent of oxygen), a small volume of a gas still remained, which was neither nitrogen nor oxygen, but some new gas which he could not identify.

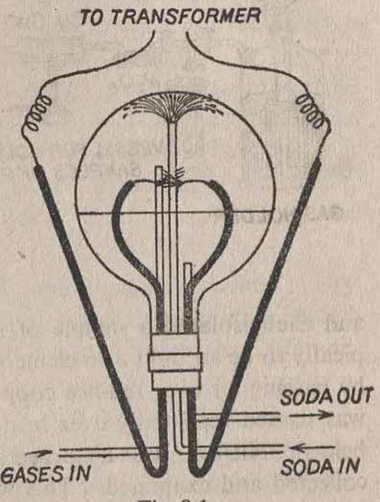

Fig. 8.1

*Discovery of Helium.*—The first positive indication of a new element came nearly 100 years later (1864), when spectroscopic evidence of the solar chromosphere showed the presence of a new *yellow* line near the $D_1$ and $D_2$ lines of sodium, but, nevertheless, distinct from them. This line was subsequently observed in the solar spectrum independently by Jansen, Frankland and Lockyer, who recognised the new line in the spectrum as the indication of a hitherto unknown element, called **HELIUM** (from *Helios*, the Sun). In 1881, Palmieri observed the same line in the spectrum of gases from Mount Vesuvius, the first known terrestrial observation of it.

While in search for other sources for helium, Hildebrand (1889) reported that, when the mineral *cleveite* was heated with dilute sulphuric acid, an unknown gas was liberated. In 1895, Ramsay examined the gas obtained from the mineral *cleveite* and found not only argon, but he also observed a yellow spectral line which Crookes confirmed as due to helium. This was the first reported recovery of helium.

*Discovery of Argon.*—The remaining monatomic rare gases were discovered by Rayleigh and Ramsay during a systematic search, following Rayleigh's demonstration that atmospheric nitrogen (*i.e.* the residue when all oxygen is removed from air by chemical means) was more dense than that produced by any chemical reaction, *e.g.* from ammonia *etc.* Ramsay first suggested (1894) a heavier constituent, and each isolated a sample of it, which Crookes showed spectroscopically to be an unknown element. Ramsay carried out his experiment by passing air over red-hot copper first, and then the residual nitrogen was passed repeatedly over heated magnesium as shown in the figure below. Nitrogen was absorbed as $Mg_3N_2$ and the unabsorbed gas was collected and examined. This was found to be monatomic and inert, of atomic weight 40, and was confirmed as Cavendish's *unreacted residue* and was called **ARGON** (the *lazy one*).

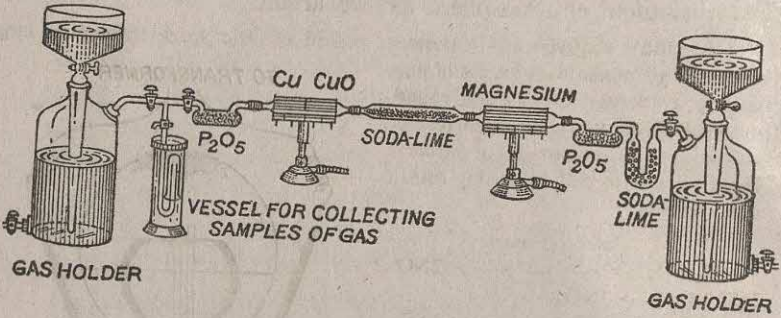

Fig. 8.2

*Discovery of Krypton.*—Two years later, Ramsay predicted another element of atomic weight between those of helium and argon, and searched for it in liquid air, boiling a large sample of it to a small volume, evaporating it and chemically removing all oxygen and nitrogen. The residue was shown spectroscopically to be a new element and the atomic weight was found to be 80. This was called **KRYPTON** (the *hidden one*), but obviously, it was not the gas predicted by Ramsay.

*Discovery of Neon and Xenon.*—In 1898, Ramsay and Travers collected some argon, the residue from air, from which nitrogen and oxygen had been removed by electric sparks and chemical reactions, and distilled it, collecting the light fraction. This gave an astonishingly brilliant red discharge. The spectroscope showed in it yet another new element, **NEON** (the *new one*). This was the gas Ramsay had foretold, having atomic weight 20. Finally in the same year, Ramsay and Travers fractionated krypton, thus isolating **XENON** (the *stranger*) of atomic weight 128.

The last member of the inert gases, *viz.* **RADON**, was discovered by Dorn (1900) as one of the products of disintegration of radium.

**ISOLATION OF INERT GASES FROM AIR.**—With the exception of helium, which is available in *natural gas* in appreciable quantities, virtually all other non-radioactive inert gases are present in air in *ppm* (parts per million) quantities by volume, although only argon can be counted as a major constituent. The three main components, $N_2$, $O_2$ and Ar, have rather similar physical properties, including a fairly narrow range of boiling temperatures.

The noble gases are isolated by removing $O_2$ and $N_2$ from air free from $CO_2$, water vapour and dust particles. This can be done either by (i) **the Chemical method** or (ii) **the Physical method.** The chemical method depends on the removal of $O_2$ and $N_2$ by means of compound formation, while the physical method works on their removal by the fractional distillation of liquid air.

**(i) The Chemical methods : Ramsay and Rayleigh's method** : Dry and $CO_2$-free air is repeatedly passed over heated copper and heated magnesium in succession, when oxygen is removed as CuO and nitrogen as $Mg_3N_2$. The residual gas contains the noble gases in a mixture. (See Fig. 8.2)

In a separate method, also adopted by Ramsay and Rayleigh, a mixture of air and oxygen in the volume ratio of 9 : 11 is admitted into a large glass globe continuously. This is subjected to electric discharge at 6000-8000 volts when $N_2$ and $O_2$ combine to form oxides of nitrogen. The supply of gas-mixture into the flask and the electric sparking are stopped. The acidic oxides of nitrogen are dissolved in a solution of NaOH which is continuously circulated through the flask. Any excess oxygen is dissolved by introducing alkaline pyrogallate solution into the flask. The unabsorbed mixture of noble gases is pumped out and collected. (See Fig. 8.1.)

**In the Fisher-Ringe's method,** dry and $CO_2$-free air is passed over a mixture of 90 parts of $CaC_2$ and 10 parts of anhydrous $CaCl_2$, kept in an iron tube and heated to 800°C. $O_2$ and $N_2$ of air are removed by the following reactions :

$$CaC_2+N_2=CaNCN+C$$
$$C+O_2=CO_2$$
$$2CaC_2+3CO_2=2CaCO_3+5C.$$

The outcoming gas-mixture is then passed over heated CuO to oxidise any unconverted CO to $CO_2$. Carbon dioxide is then absorbed in KOH solution. The resultant gas, consisting of the mixture of noble gases, is dried by passing through conc. $H_2SO_4$ and $P_2O_5$ and collected over mercury.

(ii) **The Physical method** : The isolation of inert gases from air by this method is based on the **liquefaction of air** followed by **rectification** (fractional evaporation) of liquid air when, due to the differences in boiling points, different inert gases evaporate at different temperatures. Although, it is a very complicated process, and despite the problems associated with the operation of large plants at low temperatures (about 200°C below room temperature), the process of separating air into its components by cooling, liquefying and rectifying it, has been carried out economically on an industrial scale. About one million tons of air are treated in this way each day throughout the world. Oxygen was the original important product of interest, but nitrogen and argon are also now finding wide applications. The other inert gases are obtained in the process as valuable by-products, albiet the quantities involved are very small.

**Liquefaction of Air.**—The liquefaction of air involves the following *two* operations :

(i) Purification of feed air, (ii) Cooling of the air by compression in turbine machines and expansion through valves, as well as by heat-exchange between gaseous product streams and feed air. [Air pressure used is about 200 atmospheres.]

Two processes are generally used for the liquefaction of air. These are (i) *Linde's process* and (ii) *Claude's process*.

(i) **Linde's Process.**—This process is based on the principle of lowering of temperature of gases by *Joule-Thomson effect*, together with that of *regenerative cooling.**

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* Compressed gases generally cool down when they are allowed to expand through a small orifice (*Joule-Thomson effect*). But, the extent of cooling by this process is rather small. This lowering of temperature can, however, be intensified if the gases cooled by the above process are circulated round the incoming gases, so that the latter are further cooled down before being subjected to Joule-Thomson effect. The incoming gases, therefore, undergoes expansion at a lower initial temperature and, as a result, there occurs a large drop of temperature of the gases due to the fact that the lower the initial temperature the greater is the extent of Joule-Thomson cooling. The cooled gases obtained at this stage are again circulated round the incoming gases so that the cooling effect gradually accumulates and as a result of this cumulative cooling, the gases eventually cool to their liquefying temperature. This process is known as *regenerative cooling*.

Linde's process for the liquefaction of air is shown schematically in fig. 8.3. Air is compressed to about 20 atmospheres by a compressor $P_1$ and passed through a coil cooled in a water-bath (W), a caustic soda tower ($T_1$) and a dehydrating tower ($T_2$) to another compressor $P_2$. [The water-bath removes the heat due to the compression of the air and the towers $T_1$ and $T_2$ purify the air by removing $CO_2$ and water-vapour.] The compressor $P_2$ presses the air to about 200 atmospheres and passes it through a coil immersed in a freezing chamber (F), when it cools down to about −20°C. This cooled, compressed gas is then passed through the regenerative coil (R) [this coil is enclosed in a double-walled vacuum chamber for thermal insulation] and expands through the nozzle $V_1$, when it undergoes Joule-Thomson's cooling. This cooled gas is allowed to pass round the coil R for regenerative cooling purpose and is again sent to the regenerative coil at 200 atmosphere pressure through $P_2$. On repeating these cyclic operations, the liquefying temperature of air is reached and it is transformed into the liquid. Liquid air is collected in Dewar flask (D) by opening the stop-cocks, $S_1$ and $S_2$.

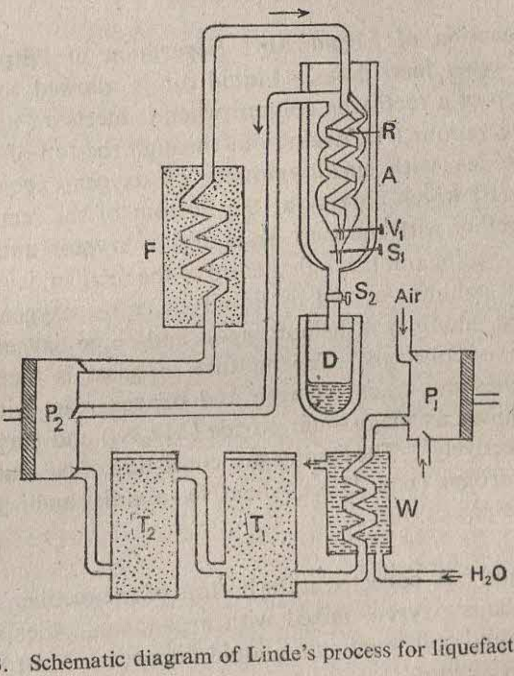


Fig. 8.3. Schematic diagram of Linde's process for liquefaction of air.

(ii) **Claude's Process.**—In this process, the liquefaction of air is effected by cooling it through *adiabatic* expansion. In an adiabatic expansion, the compressed gas is allowed to do work by expansion against external pressure, when they are cooled because of the fact that the energy required for the above work is extracted from the system itself. The schematic diagram of Claude's process is shown in fig. 8.4. The compressed air is allowed to pass through a regenerative cooling tube R (acting on Joule-Thomson effect) and the flow is divided into two parts at a point P. One part of cooled air goes to the expansion chamber (C), where it does work against external pressure and is thus further cooled by adiabatic expansion. This cooled gas then enters the heat-exchanger (E) where it meets the other part of air introduced from P. The combined air thus becomes sufficiently cooled and is ultimately liquified under pressure.

Claude's process is a more efficient one than Linde's process and it is provided with arrangements in which liquefaction of air and the fractionation of the liquid are effected simultaneously. Fractionation is carried out in elaborate rectifying columns.

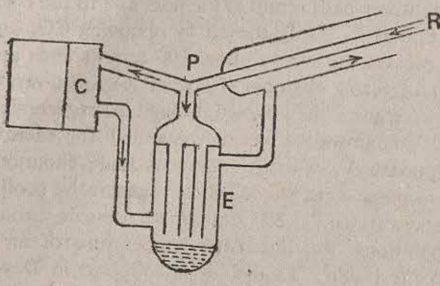


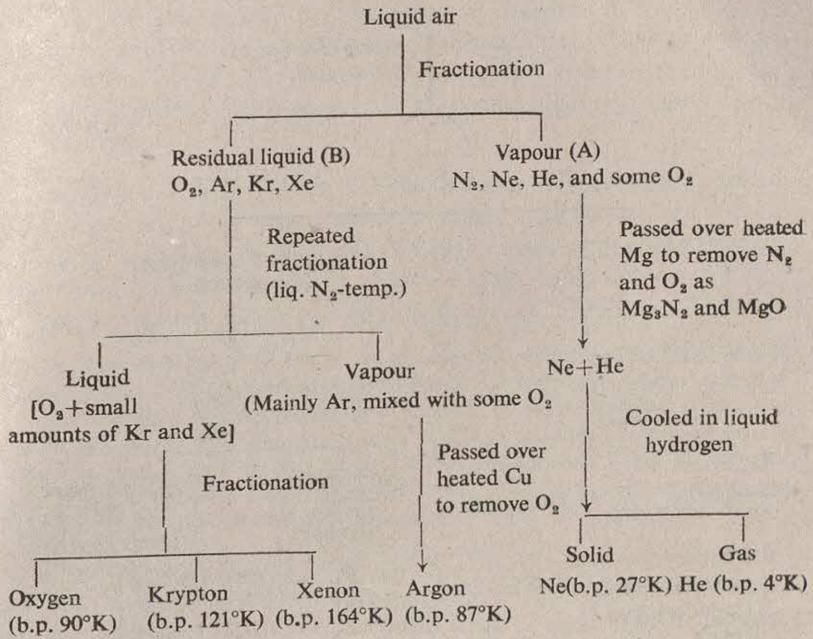
Fig. 8.4

**Fractionation of Liquid Air : Separation of Nitrogen, Oxygen, Argon and other inert gases.**—Liquid air is allowed to trickle down from the top of a rectifying column when it meets an up-going stream of air. The vapour (A), issuing out through the top of the rectifier, is mainly nitrogen with small amounts of oxygen, neon and helium. The liquid (B) which collects at the bottom of the rectifier is mainly oxygen, together with the inert gases argon, krypton and xenon. The vapour (A), issuing out through the top of the rectifier, is passed through long vertical columns cooled by liquid air, when oxygen is condensed and nitrogen, along with helium, neon and some oxygen escapes and the mixture is collected. The mixture of gases is then passed over heated magnesium, when nitrogen and oxygen react with magnesium and are retained as magnesium nitride ($Mg_3N_2$) and magnesium oxide (MgO) respectively. The issuing gas, consisting of Ne and He, is cooled in liquid hydrogen (b.p. 23°K), when Ne solidifies and is thus removed and pure He passes out.

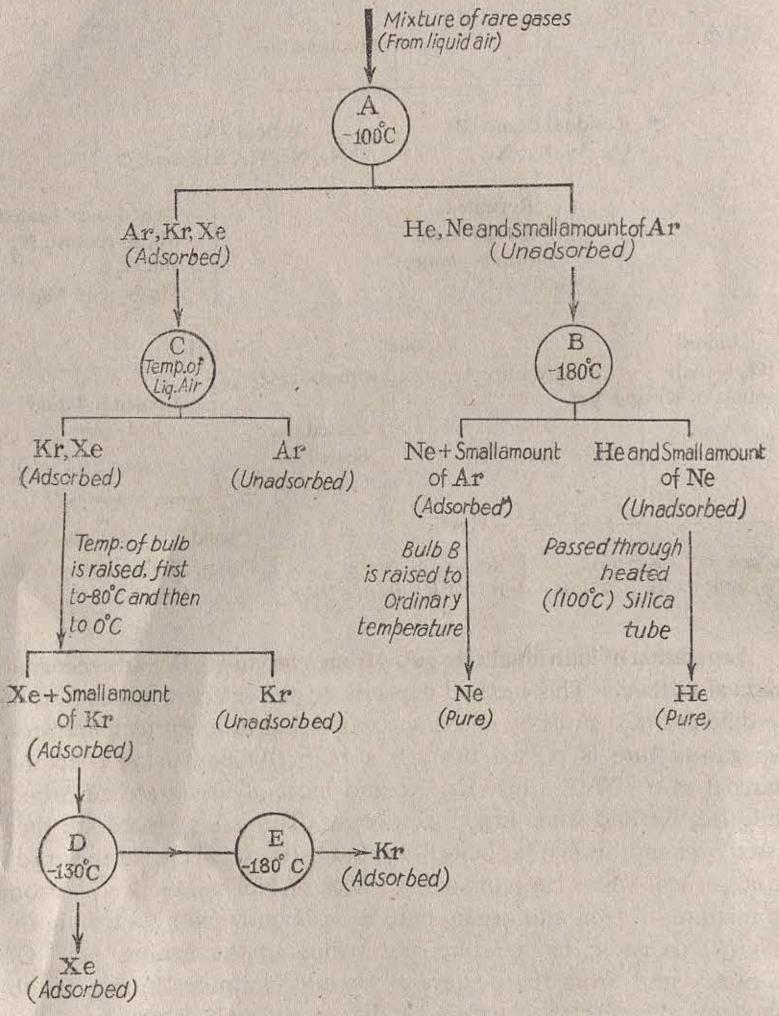
The liquid (B), collected at the bottom of the rectifier, is evaporated and the gaseous oxygen, mixed with argon, and other inert gases is circulated round coils containing liquid nitrogen. Most of the oxygen condenses to a liquid here and argon comes out as a gas. The last traces of oxygen in argon are removed by passing the mixture over heated copper.

The liquid oxygen obtained during the above operation is evaporated to a small volume to get a residual liquid rich in Kr and Xe, which are separated through fractionation.

The operations described above may be summarised in the following flow-sheet :


Liquid air
Fractionation
Residual liquid (B)
$O_2$, Ar, Kr, Xe
Vapour (A)
$N_2$, Ne, He, and some $O_2$
Repeated fractionation (liq. $N_2$-temp.)
Passed over heated Mg to remove $N_2$ and $O_2$ as $Mg_3N_2$ and MgO
Liquid
[$O_2$+small amounts of Kr and Xe]
Vapour
(Mainly Ar, mixed with some $O_2$
Ne+He
Cooled in liquid hydrogen
Fractionation
Passed over heated Cu to remove $O_2$
Solid
Gas
Oxygen (b.p. 90°K)
Krypton (b.p. 121°K)
Xenon (b.p. 164°K)
Argon (b.p. 87°K)
Ne(b.p. 27°K)
He (b.p. 4°K)

**Separation of individual rare gases from a mixture : Dewar's cocoanut charcoal method.**—This method depends on the selective adsorption of the different rare gases by cocoanut charcoal at different temperatures. The gas-mixture is passed through a bulb (A) containing cocoanut charcoal at −100°C, when Kr, Xe and most of argon are adsorbed, while He, Ne and some argon pass over. The issuing gases are then passed over another similar bulb(B) kept at −180°C, where Ne and argon are adsorbed, while He (containing traces of Ne) passes over. From the mixture of neon and argon, pure neon is obtained by warming the bulb (B) to room temperature and removing the issuing gas. On the other hand, from the mixture of He and Ne, pure He may be obtained by allowing the mixture to diffuse through a quartz tube at 1100°C. Now, the mixture of argon, krypton and xenon, which remain adsorbed in bulb (A), is separated as follows : The bulb (A) is connected to another charcoal-bulb (C) kept at −190°C (liquid air temperature), when argon passes on into this bulb and is thus removed. The bulb (A), containing now only adsorbed Kr and Xe, is warmed to −80°C, when most of Kr is set free as a pure product. On warming the bulb further to 0°C, a mixture of Xe and residual Kr is liberated. This mixture is then passed through two charcoal-bulbs kept in succession at $-150°C$ (bulb D) and at $-180°C$ (bulb E) respectively. Xenon is absorbed in the bulb (D) and krypton in the bulb (E). The pure gases are then collected by warming up the respective bulbs.



**Isolation of helium from natural gases :** In the United States, helium is commercially obtained from natural gases which contain upto 8% of the gas in admixture with mostly $N_2$, methane and other hydrocarbons. After removal of $CO_2$, if any, from the natural gas by treatment with limewater, the gas-mixture is chilled in heat-exchnagers to remove moisture and some higher hydrocarbons. Further cooling at the liquid air temperature under high pressure liquefies the remaining hydrocarbons and nitrogen. The residual gas is almost pure (98%) helium.

**Isolation of helium from certain minerals** : When the mineral *cleveite* or *monazite* is heated alone at about 1000°C, or the minerals are heated with dilute $H_2SO_4$, helium which remains entrapped in them is set free. The evolved gas is collected after passing through KOH solution (to remove $CO_2$) and then through conc. $H_2SO_4$ (to dry it).

**Isolation of radon** : Radon is the product of radioactive disintegration of radium and has a half-life period of less than 4 days. It may be obtained by acidifying an aqueous solution of a radium salt and pumping out the evolved gas, which may contain Rn along with $H_2$, $O_2$, moisture, $CO_2$, $N_2$ and He. $H_2$ and $O_2$ are removed by sparking (to produce $H_2O$), $CO_2$ by passing over KOH, moisture by $P_2O_2$. The residual gas is cooled when Rn freezes, while $N_2$ and He escape as gas. The frozen Rn, which readily becomes gaseous on raising the temperature, is collected.

**Physical properties of the rare gases** : The rare gases are all colourless and possess no smell or taste. They are slightly soluble in water, and the solubility increases with the increase of their atomic number. It is relatively difficult to liquefy them and the ease of liquefaction increases with their atomic numbers. The boiling points of the liquefied gases increase with the increase of their atomic numbers. The gases are all monatomic and as such, their molecular weights are the same as their atomic weights. This is evidenced by the value of the ratio of the specific heats $Cp/Cv$ of the gases, which is 1.667, and also from the values of their refractive indices, dielectric constants *etc*. The liquefied gases can be transformed into the solid state by a comparatively small further diminution in temperature. All these gases are absorbed by cocoanut charcoal at low temperatures.

The rare gases give rise to characteristic spectral lines, by means of which they can be readily identified. The last member of the series, *viz*. radon, is radioactive.

## Chemical behaviour of the Rare Gases.

The most stable electronic configuration of the outermost shell of the atoms of rare gases, resulting in the complete pairing of all the electrons present there, and the absence of any bonding orbital, together with the very high ionization potential and negligible electron affinity of their atoms, have made them chemically inactive or inert. Usual chemical methods failed to make them undergo combination with other elements to form compounds in the true sense of the term. However, a number of so-called *compounds* of rare gases has been reported in literature from time to time.

(A) One such class of **compounds** are **hydrates** and **deuterohydrates** of the composition, $G.xH_2O$ and $G.yD_2O$, where G is an inert gas other than He and Ne and $x$ and $y$ are often 6. These are formed as colourless crystals at high pressure and low temperatures, but are not very stable. Such combinations are regarded as possible through **dipole-induced diplole attraction.** In the presence of a sufficiently strong dipole like $H_2O$, $D_2O$ *etc.* an inert gas atom is polarised to act as dipole itself, and hence the attraction for the original dipole. Such attraction is also responsible for the formation of phenol derivatives of the rare gases, such as $Kr.2C_6H_5OH$, $Xe.2C_6H_5OH$ and $Rn.2C_6H_5OH$.

(B) **Clathrate or Enclosure compounds : Compounds formed by physical trapping.**—The most important and most easily prepared *compounds* of the rare gases are those in which the gases are trapped within cavities or holes in the crystal-lattices of some organic or inorganic compounds. Thus, crystallisation of solutions of quinol (*p*-dihydroxybenzene) under an inert gas pressure of 10-14 atmospheres, produces crystals which contain the inert gas trapped in the lattice of quinol. The inert gas is released on dissolving or heating the crystals ; otherwise, the crystals are stable for years. It has been observed that 3 molecules of quinol are required to form the clathrate or the cage ; as such, the limiting ratio of quinol to the trapped atom of the inert gas for the composition of the compound should be 3 : 1. But, due to incomplete filling of the cages, the ratio may alter. Further, the free diameter of the quinol cage is $\sim$ 4Å. So, an atom of an appropriate size will only be trapped in it. Helium and neon do not form quinol-clathrates due to their smaller sizes, as they can easily escape between the atoms of the quinol molecules which form the cage.

It may be mentioned that the hydrates and deuterohydrates of inert gases, as described under (A), are also enclosure compounds, the $H_2O$ or $D_2O$ molecules acting as the host lattice.

(C) **Compounds formed through coordination** : The existence of free electron-pairs in an atom of an inert gas would suggest its capability of forming coordination complexes with powerful electron pair acceptors. Booth and Wilson (1935) suggested from their studies on freezing point determinations of various mixtures of argon and boron trifluoride that, compounds containing 1, 2, 3, 6, 8 and 16 moles of $BF_3$ per mole of argon were formed. Although the compounds containing upto three $BF_3$ molecules per atom of argon could be formulated as the inert gas atom donating 3 pairs of electrons to the three boron atoms, the formulation of compounds containing 6, 8 or 16 $BF_3$ molecules per argon atom necessitated the donation of lone pairs of electrons of the F atoms of $BF_3$ to other boron atoms, as shown in the fig. 8.5 for A. 8 $BF_3$ as an example.

Objections to such formulations were raised by Wiberg and Karbe (1948) on the ground that boron trifluoride does not polymerise among their own molecules (as shown in the formulation) under any condition. They also showed that argon, krypton and xenon were immiscible with $BF_3$ in the liquid state and no such compounds as suggested by Booth and Wilson are formed.

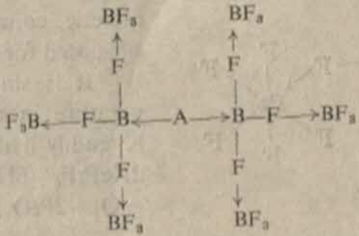


Fig. 8.5

(D) **Compound-formation under excited conditions** : Informations regarding the formation of compounds by inert gases under exited conditions are available only for helium, where the unpairing of 1*s* electrons and its promotion to 2*s* state by thermal methods would result in the appearance of chemical activity of the element. In a glow-discharge, mercury helide ($HgHe_{10}$) has been reported to be formed as a more or less stable product ; electron bombardment of tungsten in an atmosphere of helium produces tungsten helide ($WHe_2$). Formation of unstable helides of Bi, Tl, In, Zn, Na, K, Rb, Pt, Pd, Fe, U, I, S and P has also been reported. Metal electrodes like Pt, Pd, Fe *etc.*, when used in discharge tubes containing inert gases, often absorb stoichiometric amounts of these gases, and compounds like $Pt_3He$, FeHe, PdHe, FeA *etc.* have been isolated.

(E) **True compounds of Rare gases** : Considering the values of ionization potential and electronegativity of Kr, Xe and Rn, relative to those of oxygen and fluorine, Pauling predicted (1933) that these rare gases should combine chemically with them to form compounds of the type $KrF_6$, $XeF_8$, $H_4XeO_6$, $Ag_2XeO_4$ and so on. The prediction proved true when the first compound of xenon, $XePtF_6$ was isolated as a yellow solid (Bartlet, 1962). $XePtF_6$ is actually the *first* true compound of a noble gas to be synthesised. Its preparation showed that there is nothing special about this group of elements so far the compound-formation is concerned. The relative lack of their chemical reactivity is the outcome of the very stable electronic configuration and the high ionisation potential of their atoms.

**Preparation of $XePtF_6$** : This is obtained as a yellow solid when the deep red vapours of $PtF_6$ react with xenon at ordinary temperatures : $Xe+PtF_6=XePtF_6$. (This reaction is actually the oxidation of xenon atom by $PtF_6$). Further investigations on the product revealed that it was actually a compound of pentavalent platinum, having the composition $Xe(PtF_6)_2$, and a flourine-bridged structure of two $PtF_5$-moieties connected by $XeF_2$ was proposed for it.

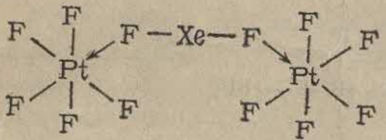


Fig. 8.6

It is stable at room temperature in the dry state, but is readily hydrolysed by water : $2XePtF_6+6H_2O = 2Xe+12HF +O_2+2PtO_2$.

[Similar compounds were later prepared by the interaction of xenon and the hexafluorides like $PdF_6$, $RhF_6$, $RuF_6$ *etc.* and all of them have the composition $Xe(MF_6)n$, where M is a metal of Group VIII and *n* is generally 2. Compounds of the type $XeZF_6$, where Z is P, Sb and Si have also been prepared through the interaction of xenon, fluorine and the fluoride ($PF_5$, $SbF_5$, $SiF_4$) of the other element, Z. Of these, $XePF_6$ and $XeSiF_6$ decompose at room temperature while $XeSbF_6$ is quite stable at this temperature.]

Quite a number of fluorides, oxides and oxyfluorides of xenon has been prepared and characterised. Some fluorides of krypton and radon have also been prepared. But, similar compounds of helium, neon and argon have not yet been isolated, and this is probably due to the too high ionisation potential values of their atoms. In general, the krypton compounds are less stable than the corresponding xenon compounds, probably due to the higher ionisation potential and smaller size of the krypton atom. The radon compounds are too unstable to be studied on account of their α-ray emission.

### Compounds of Xenon.

**Fluorides** : Three simple fluorides of xenon are known with certainty. These are : xenon difluoride ($XeF_2$), xenon tetrafluoride ($XeF_4$) and xenon hexafluoride ($XeF_6$).

### Xenon difluoride ($XeF_2$).

*Preparation* : Xenon difluoride was first obtained by exposing an equimolecular mixture of xenon and fluorine to ultra-violet light. An almost quantitative yield of $XeF_2$ is obtained by the interaction of xenon and excess of $O_2F_2$ at $-118°C$.

*Properties* : Xenon difluoride is a colourless crystalline solid that melts at 120°—140°C. It is least volatile among the fluorides of xenon and the pure compound is quite stable when dry. It is soluble in liquid hydrofluoric acid without any change.

$XeF_2$ is a strong oxidising agent. It oxidises hydrogen and water : $XeF_2+H_2=Xe+2HF$ ; $2XeF_2+2H_2O=2Xe+4HF+O_2$.

It is easily hydrolysed by an aqueous solution of a base : $2XeF_2+4NaOH=2Xe+4NaF+2H_2O+O_2$.

In acidic solution, the hydrolysis is slow and the resultant solution has a pungent odour and strong oxidising property. It dissolves in molten $SbF_5$ to produce $Xe(SbF_6)_2$ :

$$XeF_2+2SbF_5=Xe(SbF_6)_2.$$

### Xenon tetrafluoride ($XeF_4$).

*Preparation* : Xenon tetrafluoride was prepared (1962) by heating a mixture of xenon and $F_2$ in 1 : 5 molecular proportion for a few hours at 400°C and under 6 atmospheres pressure. The gaseous product was then suddenly cooled to $-78°C$ and excess of $F_2$ was pumped off.

*Properties* : $XeF_4$ is a colourless crystalline solid, melting at about 100°C. The substance is volatile and it sublimes on heating in a current of nitrogen. It is quite stable in the pure and dry state. It dissolves unchanged in liquid HF, but dissolves in molten $SbF_5$ and $TaF_5$ to form solid compounds :

$$XeF_4+2SbF_5=Xe(SbF_6)_2+F_2$$
$$XeF_4+2TaF_5=Xe(TaF_6)_2+F_2.$$

It oxidises hydrogen, $BCl_3$ and KI and is itself reduced to xenon :

$$XeF_4+2H_2=Xe+4HF$$
$$3XeF_4+4BCl_3=3Xe+4BF_3+6Cl_2.$$
$$XeF_4+4KI=Xe+2I_2+4KF.$$

$XeF_4$ is a strong fluorinating agent and it fluorinates sulphur tetrafluoride to hexafluoride :

$$XeF_4+2SF_4=Xe+2SF_6.$$

On hydrolysis with water,* it is transformed into Xe and xenon trioxide ($XeO_3$), the latter being obtained as a solid on evaporating the aqueous solution :

$$6XeF_4+12H_2O=4Xe+2XeO_3+24HF+3O_2.$$

In strong alkaline solutions, the above hydrolysis results in the formation of alkali perxenates, through the intermediate formation of $HXeO_4^-$.

$$XeO_3+NaOH=NaHXeO_4$$

$$2NaHXeO_4+2NaOH=\underset{\text{(Sodium perxenate)}}{Na_4XeO_6}+Xe+O_2+2H_2O$$

[Barium perxenate ($Ba_2XeO_6$), lead perxenate ($Pb_2XeO_6$) and silver perxenate ($Ag_4XeO_6$) have been prepared from sodium perxenate by double decomposition. Perxenate solutions are powerful oxidising agents.]

**Xenon hexafluoride ($XeF_6$).**

*Preparation* : Xenon hexafluoride was obtained by heating a mixture of Xe and $F_2$ in 1 : 20 molecular proportion for about 16 hours at 300°C and under a pressure of 60 atmospheres. It is also formed by the interaction of $XeF_4$ and $O_2F_2$ at $-130$°C :

$$XeF_4+O_2F_2=XeF_6+O_2.$$

*Properties* : $XeF_6$ is a colourless crystalline solid. It turns yellow when heated to 43°C and melts at 48°C to give a yellow liquid. It is more volatile than the other two fluorides of xenon. It is stable at room temperature.

Xenon hexafluoride dissolves in liquid HF with the formation of $XeF_5^+$ and $HF_2^-$ ions :

$$XeF_6+HF \rightleftharpoons XeF_5^+ + HF_2^-.$$

It oxidises hydrogen like the other xenon fluorides :

$$XeF_6+3H_2=Xe+6HF.$$

It is hydrolysed by water, the final product of hydrolysis being $XeO_3$ and HF :

$$XeF_6+3H_2O=XeO_3+6HF.$$

On partial hydrolysis, xenon oxyfluoride ($XeOF_4$) is formed :

$$XeF_6+H_2O=XeOF_4+2HF.$$

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*It is a complicated disproportionation reaction which is represented by the given equation for the sake of simplicity.

In strongly alkaline medium, the hydrolysis of $XeF_6$ finally produce alkali perxenates and xenon, probably through the intermediate formation of xenate ion ($HXeO^-_4$) :

$$XeF_6+7OH^- \rightarrow HXeO^-_4+3H_2O+6F^- ;$$
$$2HXeO^-_4+2OH^- \rightarrow \underset{\text{(perxenate)}}{XeO_6^{-4}}+Xe+2H_2O+O_2.$$

It readily reacts with silica to form $XeOF_4$ and $SiF_4$. So, it cannot be stored in glass vessels.

$$2XeF_6+SiO_2=2XeOF_4+SiF_4.$$

It reacts with molten rubidium fluoride and cesium fluoride to produce the corresponding heptafluoroxenates which decompose easily into the octafluoroxenates :

$$XeF_6+RbF = RbXeF_7$$
$$XeF_6+CsF = CsXeF_7$$
$$2RbXeF_6 = XeF_4+Rb_2XeF_8.$$

The octafluoraxenates are very stable compounds which decompose above 400°C.

[Sodium fluoride and potassium fluoride form the corresponding octafluoroxenates directly on reacting with $XeF_6$. But, they are less stable than the corresponding rubidium and cesium salts.]

The Xe-F bond energy in the xenon fluorides is about 30 KCal/mole.

**Xenon Oxides :**

**Xenon trioxide ($XeO_3$).**

*Preparation* : $XeO_3$ is formed in solution when $XeF_4$ or $XeF_6$ is hydrolysed with water. The aqueous solution gives $XeO_3$ on evaporation.

$$6XeF_4+12H_2O=2XeO_3+24HF+4Xe+3O_2$$
$$XeF_6+3H_2O=XeO_3+6HF.$$

*Properties* : $XeO_3$ is a white, non-volatile solid and is highly explosive when dry. It is quite stable in aqueous solution which is acidic in nature and is known as *xenic acid* :

$$XeO_3+H_2O \rightleftharpoons \underset{\text{(xenic acid)}}{H_2XeO_4} \rightleftharpoons H^++HXeO^-_4.$$

In alkaline solution, it disproportionates into free xenon and perxenate :

$$4XeO_3+12NaOH=Xe+3Na_4XeO_6+6H_2O.$$

Xenic acid (or xenates and perxenates) is as strong an oxidising agent as ozone.

**Xenon tetroxide ($XeO_4$).**

*Preparation* : When sodium perxenate is treated with conc.$H_2SO_4$, xenon tetroxide is formed :

$$Na_4XeO_6+2H_2SO_4=2Na_2SO_4+XeO_4+2H_2O.$$

*Properties* : $XeO_4$ is an unstable gas at room temperature. It can be transformed into a yellow solid at very low temperature. It explodes even at $-40°C$.

**Oxyfluoride of Xenon :**

**Xenon oxyfluoride ($XeOF_4$) :**

*Preparation* : It is formed when $XeF_6$ is partially hydrolysed by water :

$$XeF_6+H_2O=XeOF_4+2HF.$$

It can also be prepared by the action of $XeF_6$ on silica :

$$2XeF_6+SiO_2=2XeOF_4+SiF_4.$$

*Properties* : Xenon oxyfluoride ($XeOF_4$) is a colourless volatile liquid that solidifies at about $-28°C$. It is stable at room temperature and is somewhat more volatile than $XeF_6$. It reacts with water to form $XeO_3$ as the final product :

$$XeOF_4+2H_2O=XeO_3+4HF.$$

A chart, showing the important compounds of Xenon, is given below :

| Oxidation sate of Xe | Compound | Nature | Melting point °C | Remark |
|---|---|---|---|---|
| +2 | $XeF_2$ | colourless crystals | 140 | |
| +4 | $XeF_4$ | ,, | 114 | |
| +6 | $XeF_6$ | ,, | 47.7 | |
| ,, | $XeOF_4$ | colourless liquid | —28 | |
| ,, | $XeO_3$ | colourless crystals | — | Explosive |
| +8 | $XeO_4$ | colourless gas | — | Explosive |

**Compounds of Krypton.**

**Krypton fluorides** : Two different fluorides of krypton, *viz.* $KrF_2$ and $KrF_4$ have been reported in literature. But, there is much doubt about the authenticity of $KrF_4$.

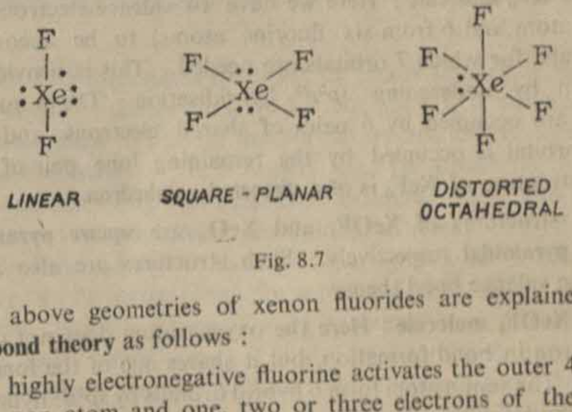
**Krypton difluoride ($KrF_2$)** : It is formed when a mixture of Kr and $F_2$ is subjected to electric discharge, or when a mixture of the two gases at low pressure is irradiated.

$KrF_2$ is a white crystalline solid. It sublimes below 0°C and decomposes at room temperature. It is highly reactive and is a good fluorinating agent. It is hydrolysed by water at $-80°$ to $-60°C$ to produce so-called *kryptic acid*, of which little is known. It combines with $SbF_5$ to form a more stable and less volatile double salt, $KrF_2.SbF_5$.

**Compounds of Radon** : Fluorides of radon, *viz.* $RnF_2$ and $RnF_4$, have also be reported. But, later studies have doubted their composition. Theoretically, however, the formation of the oxides and chlorides of radon is also possible.

**Structures of the compounds of Xenon.**

The following structures of the xenon fluorides have been found by the electron diffraction and infra-red spectral studies :



LINEAR

SQUARE - PLANAR

DISTORTED OCTAHEDRAL

Fig. 8.7

The above geometries of xenon fluorides are explained by the **valence bond theory** as follows :

The highly electronegative fluorine activates the outer 4*d* orbitals of the xenon atom and one, two or three electrons of the filled 5*p* orbitals of it are promoted there. This gives rise to 2, 4 or 6 half-filled valence-orbitals in the xenon atom which can now undergo required type of hybridisation and form covalent bonds with 2, 4 or 6 fluorine atoms, and the compounds $XeF_2$, $XeF_4$ and $XeF_6$ are thus formed.

(i) **$XeF_2$ molecule** : Here we are to deal with 10 valence-electrons (8 from the valence-shell of xenon atom and 2 from the two fluorine atoms) and they are to be filled in orbitals. Five orbitals are needed for the purpose and these are provided by the $sp^3d$ hybridisation of the xenon atom. These 5 hybrid orbitals are directed in space towards the five corners of a trigonal bipyramid. Two of these 5 hybrid orbitals contain the two shared pairs of electrons and the other three hybrid orbitals are occupied by the three lone pairs of the xenon atom. For the greatest stability of the molecule, the two shared pairs of electrons lie as far apart from each other as possible, making the Fe—Xe—F angle 180°. Thus, the structure of $XeF_2$ is *linear.*

(ii) **$XeF_4$ molecule** : In this case, 12 valence-electrons (8 from the Xe atom and 4 from the four F atoms) are to be properly accommodated in orbitals, for which 6 orbitals are required. These are provided by the Xe atom by undergoing $sp^3d^2$ hybridisation. The six hybrid orbitals are directed in space towards the 6 corners of an octahedron. The four hybrid orbitals which lie in one plane with the Xe atom are occupied by the 4 shared pairs of electrons, so that the four F atoms lie in one plane along with the central Xe atom. The two lone pairs of the Xe atom occupy the two hybrid orbitals, one above and one below the plane containing Xe and 4 fluorine atoms. Thus, the structure of $XeF_4$ is **square planar**.

(iii) **$XeF_6$ molecule** : Here we have 14 valence-electrons (8 from the Xe atom and 6 from six fluorine atoms) to be accommodated in orbitals, for which 7 orbitals are needed. This is provided by the Xe atom by undergoing $sp^3d^3$ hybridisation. The 6 such hybrid orbitals are occupied by 6 pairs of shared electrons and the 7th hybrid orbital is occupied by the remaining lone pair of Xe atom. So, the structure of $XeF_6$ is of a **distorted octahedron**.

The structures of **$XeOF_4$** and **$XeO_3$** are **square pyramidal** and **trigonal pyramidal** respectively. Such structures are also accounted for by the valence bond theory.

(iv) **$XeOF_4$ molecule** : Here the oxygen atom does not contribute any electron in bond formation, but it shares one of the lone pairs of Xe atom. The xenon atom form 6 hybrid orbitals by $sp^3d^2$ hybridisation. The 6 hybrid orbitals are directed in space towards the six corners of an octahedron. Four such orbitals, lying in the same plane as the central Xe atom, are occupied by the 4 shared pairs, forming 4 Xe—F bonds (like $XeF_4$ molecule). Of the two axial hybrid orbitals (lying above and below the above plane), one is occupied by a lone pair of Xe atom and the other orbital, containing another lone pair of Xe atom, is replaced by a Xe—O bond. So, the structure of the molecule is like **a square pyramid**.

(v) **$XeO_3$ molecule**: In this case also oxygen atoms do not contribute any electron for bond formation, but shares 3 of the 4 lone pairs of Xe, producing three Xe—O bonds. Here we are to accommodate 8 **electrons** (of the Xe atom only) in orbitals. The Xe atom is supposed to undergo $sp^3$ hybridisation. The three hybrid orbitals contain 3 bond pairs and one hybrid orbital contains the lone pair, making the structure of the molecule like **a trigonal pyramid** with the O—Xe—O bond angle 130°. [The deviation from the tetrahedral angle (109°) is due to the greater lone pair-bond pair repulsion, as compared to that of bond pair—bond pair.]

**Peculiar properties of liquid Helium*** : Helium liquefies at 4.12°K and the liquid formed behaves normally and is called He-I. On further cooling under atmospheric pressure to 2.178°K, a second form, called He-II, appears (this transition temperature is called the λ-point). He-II has very low viscosity and the liquid is super-conducting. It forms exceedingly thin films which flow practically without friction. If He-II is kept in two concentric vessels at unequal levels, it will flow from one to the other, even spreading upwards, if necessary. He-II is often referred to as *a degenerate gas, a superfluid or* the fourth state of matter, but no satisfactory explanation for such behaviour of He-II is available as yet.

**USES** : The inert gases are used for many important purposes. Helium is used in nuclear reactors for cooling. It is the main constituent of synthetic breathing gas for divers and others working in high-pressure conditions. It is widely used for producing low temperatures and for filling metereological balloons. It is also used to provide an inert atmosphere in the welding of metals and alloys that are easily oxidised. It is also used for inflating the tyres of aeroplanes. Neon is used in discharge lamps for advertising and display purposes (brilliant red colour). Argon is used to create inert atmosphere in arc-welding and in metallurgy. It is also used for filling incandescent lamps. Krypton is mainly used in filling incandescent lamps for advertising and display (very bright luminous light). Xenon is used for filling lamps (brilliant natural daylight) for photographic flash lights and in lighthouse projectors. Radon has been employed in the treatment of malignancies.

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*The peculiarities of liquid helium are shown only by the isotope $_2He^4$, and and not by the isotope $_2He^3$.

CHAPTER IX

# HYDROGEN, WATER AND HYDROGEN PEROXIDE

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## Position of hydrogen in the Periodic Table.

Among the whole host of chemical elements, hydrogen possesses unique and peculiar properties which leave the question of its placement or position in the Periodic Table open to discussion. It is usually placed in the first period of the Periodic Table along with helium, with gaps for elements with atomic weights between 1 and 4. But, the present knowledge of atomic numbers proves beyond doubt that other elements can not exist in between hydrogen (atomic number, 1) in Group IA and helium (atomic number, 2) in Group O.

The placement of hydrogen in Group IA with the alkali metals appears to be logical on account of its following similarities with the latter : (i) the monopositive valency of hydrogen, arising from the similarity of the electronic configuration of its atom with that of the alkali metals, both having a lone electron in the outermost valence-shell ; (ii) the pronounced electropositive character of hydrogen like the alkali metals, and its capacity of forming alloy with palladium, together with its notable reducing properties like those of the alkali metals. But, very conspicuous differences between hydrogen and the alkali metals are that, (a) the former is a non-metal while the latter are metals, and (b) the former is a diatomic gas while the latter are solids, mainly monatomic in the gaseous state.

The alternative placement of hydrogen in Group VIIB with the halogens, has several plausible reasons behind it. These are : (i) like halogens ($F_2$, $Cl_2$, $Br_2$ and $I_2$), hydrogen is also a non-metal consisting of diatomic molecules ; (ii) like $F_2$ and $Cl_2$, it is also a gas at ordinary temperatures, and is more difficultly liquefiable than fluorine, which justifies its position at the top of fluorine. With such placement, the difference between atomic weights of hydrogen and fluorine is 18, a value which is very near 16, the usual difference between the atomic weights of two adjacent elements of the same group occuring in the two short periods of the Periodic Table ; (iii) hydrogen forms salt-like hydrides like NaH, $CaH_2$, *etc*. which are comparable with the halides of metals like NaCl, $CaCl_2$ *etc*. [On electrolysis of these hydrides in the fused state, hydrogen is liberated at the anode, thus showing the electronegative character of hydrogen in these hydrides.] ; (iv) hydrogen can be replaced *atom for atom* by halogens in organic compounds.

The placement of hydrogen in the Periodic Table can also be considered from another point of view, *viz.* its capability of forming different types of compounds with other elements, and its justification from the electronic configuration of the atom of hydrogen. Three distinct types of compounds are formed by hydrogen. With the alkali and alkaline earth metals, it forms white, salt-like solids, in which hydrogen exhibits *negative* valency. With the non-metals like sulphur, halogen *etc.*, it forms gaseous hydrides which are acidic in aqueous solutions, producing $H^+$ ions and thus, it exhibits *positive* valency in these cases. With the elements in the middle of the periods, *viz.* carbon, silicon *etc.*, hydrogen form mainly gaseous hydrides which are non-electrolytes in behaviour and in these cases hydrogen exhibits *covalency.*

Such behaviour of hydrogen finds easy explanation when we consider that an atom of hydrogen consists of a nucleus of unit positive charge (and unit mass) surrounded by an electronic orbit containing a single electron. In combining with strong electronegative elements, this lone electron is easily removed and transferred to an atom of the latter, thus changing a hydrogen atom into a $H^+$ion. In such cases, the behaviour of hydrogen is that of a monovalent electropositive element. With strongly electropositive elements (like alkali- or alkaline earth metals), an atom of hydrogen may accept an electron so as to reach the stable electronic configuration of a helium atom. In combination with such elements, hydrogen thus behaves as a monovalent electronegative element. In the cases of gaseous hydrides of carbon, silicon *etc.*, hydrogen combines with the elements by forming covalent bonds with shared pairs of electrons, thus completing its own duet and the octets of the other element.

Recognising that, it contains in itself, the characteristics of all the different types of elements met with in the Periodic Table, hydrogen is now considered to be an element, not belonging to any one particular group in the Periodic Table, but *its proper place is at the head of the Table, as the prototype of the whole system of the elements.*

With such a background of the characteristics of hydrogen, it is thought justified to discuss its chemistry, along with two of its important compounds, *viz.* water and hydrogen peroxide, in a separate section that follows.

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## HYDROGEN

*Symbol : H* *Atomic No. : 1 ;* *Atomic Wt. : 1.008 ;*

*Electronic configuration :* $1s^1$

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Discovered by Paracelsus in the 16th Century. First prepared by Robert Boyle (1672). Cavendish (1766) recognised it as an elementary gas and Lavoisier (1783) named it hydrogen (water producer), as it forms water on combustion. It was first obtained through electrolysis of water by Nicholson and Carlisle (1789).

**OCCURRENCE** : In the elementary state, small amounts of hydrogen are found in volcanic gases and in certain rocks or minerals, where it is entrapped within the solid, and also in natural gases.

It has been found by spectroscopic analysis that large quantities of hydrogen occur in the sun and in most stars. In the atmospheric air, it occurs in traces (about 0.1 part per million). In the combined state, the element is abundant in nature as various types of compounds. Thus, in combination with oxygen, it occurs in water (ice, liquid water and water-vapour) ; with carbon, it forms components of petroleum and natural gases ; in combination with carbon, oxygen and some other elements, it is present in almost all organic substances such as wood, coal, fat, oil, sugar, animal- and vegetable- tissues and a host of other natural products.

**PREPARATION** : Hydrogen is required in large quantities for commercial and laboratory purposes, and is readily available on industrial scale. The laboratory methods of the preparation of the gas are of mainly academic interest and are rarely used for the production, except for the demonstration purposes.

For the preparation of hydrogen in the laboratory, water, acids or alkalis may be used as the starting materials. The important methods of preparation of hydrogen are given below :

I. **From water** : (a) *At ordinary temperatures*, active metals like the alkali metals (Li, Na, K, Rb and Cs) decompose water vigorously, so that the evolved hydrogen often catches fire due to the enormous heat evolved. Sodium amalgam, however, reacts quietly with water to liberate hydrogen. Alkaline earth metals (Mg, Ca Ba, Sr) decompose water slowly at ordinary temperatures, but the liberation of hydrogen is more rapid with hot water. $2Na+2H_2O=2NaOH+H_2$ ; $Ca+2H_2O=Ca(OH)_2+H_2$.

(b) *With boiling water*, metals like Ca, Mg, Al (or their amalgams) and Zn-Cu couple react to produce hydrogen.

$$2Al+6H_2O=2Al(OH)_3+3H_2.$$

(c) Heated Zn, Mg, Al, Fe, Ni, Co, Cr, Mn, Pb and Sn decompose *steam* to form the oxides of the corresponding metals, together with the evolution of hydrogen. [The hydroxides of these metals are not stable at the high temperatures used.]

The passage of steam over red-hot iron is utilised in the production of hydrogen on a large scale in **Lane Process** which was of considerable technical importance for a while. It is still used to some extent. The reaction, $3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2$, is reversible and exothermic, and is best carried out by passing steam through red-hot spongy iron (600—850°C) kept in vertical iron cylinders. Ferroso-ferric oxide produced in the reaction can be re-converted to iron by passing water gas through it and, as such, the process can be re-cycled with the same quantity of iron. $3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2$ ; $Fe_3O_4+4CO=3Fe+4CO_2$;

(d) Above 1000°C, steam reacts with coke to produce a mixture of equal volumes of CO and $H_2$ (*Water gas*) : $H_2O+C=CO+H_2$.

The gaseous products are mixed with steam and passed over a catalyst (iron oxide or cobalt oxide) at 400°C, when CO is converted to $CO_2$, producing more hydrogen. $H_2O$ (steam)$+CO=CO_2+H_2$. The $CO_2$, thus formed, is removed by washing with water under pressure, and any unconverted CO is washed by passing the gas through ammoniacal cuprous chloride solution. Hydrogen obtained by this process contains some nitrogen which can be removed by cooling with liquid air boiling at —200°C, when $N_2$ is liquefied and pure hydrogen passes over. This method is used for the manufacture of hydrogen in the **Bosch Process.**

(e) Some metallic hydrides like LiH, $CaH_2$ or $LiAlH_4$ are decomposed by water to produce hydrogen (**Hydrolith Process**).

$CaH_2+2H_2O=Ca(OH)_2+2H_2$ ; $LiH+H_2O=LiOH+H_2$.

The method is expensive, but it has advantages in field for military and metereological purposes.

(f) **Electrolysis of water** : Water is practically a non-conductor of electricity. So, for the electrolysis of water, a very dilute solution of an acid or an alkali is generally used, when hydrogen is liberated at the cathode and oxygen at the anode, in the volume-ratio 2:1.

A very pure sample of hydrogen may be prepared in the laboratory by the electrolysis of a warm solution of pure barium hydroxide in a hard glass U-tube with nickel electrodes. The hydrogen liberated at the cathode is first passed over heated platinum gauge, where oxygen from air-leaks and diffusion is burnt to water. The gas is then passed through U-tubes containing KOH and $P_2O_5$ in succession for drying. A small quantity of $N_2$, remaining in the gas, is removed by passing into an exhausted bulb containing heated palladium foil, which readily absorbs hydrogen (but not $N_2$ or any other gas). The residual gas is pumped out of the bulb, which is later heated to dull redness to take out the pure hydrogen (Fig. 9.1). This method may be used for the small-scale manufacture of pure hydrogen.

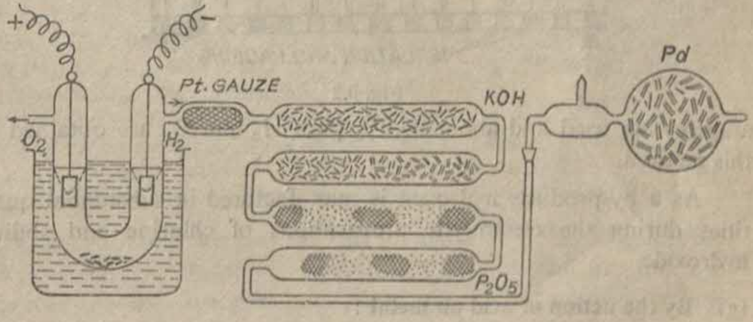


Fig. 9.1

Through this method, hydrogen is generally manufactured by the direct electrolysis of dilute sodium hydroxide or potassium hydroxide solution in a number of *bi-polar cells*, connected in series (upto 250 such cells may be connected together in an assembly), in such a way that the anode of one cell functions at the same time as the cathode in the next cell. The electrodes are of iron sheets, coated with nickel (to resist oxidation) on the anode side. Each electrode is fitted with a gas-collecting bell at the top, which are connected to two separate channels for the collection of $H_2$ and $O_2$ respectively. The electrodes are separated by porous asbestos partitions to prevent the mixing of $H_2$ and $O_2$ through diffusion. Operating currents upto 10,000 amperes are used and about 99.9% pure $H_2$ and $O_2$ are obtained by this method.

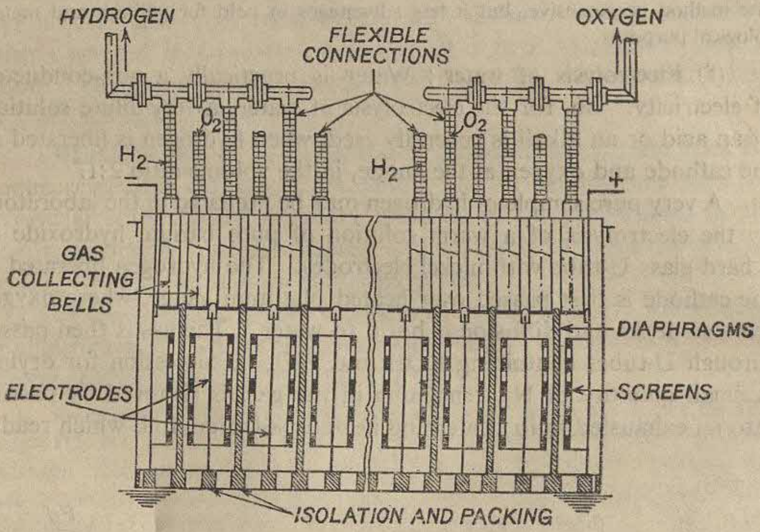


Fig. 9.2

As a by-product, hydrogen is manufactured in substantial quantities during the electrolytic preparations of chlorine and sodium hydroxide.

(g) **By the action of acid on metal :**

This process is mostly used for the preparation of hydrogen in the laboratory. Metals which are placed above hydrogen in the **electro-chemical series,** liberate hydrogen on treatment with dilute acids. (This is due to the fact that the oxidation potential of these metals are lower than that of hydrogen, and as such, they tend to be easily oxidised to the corresponding ions, liberating hydrogen by reducing the $H^+$ ions in the acids to the elemental state. As for the metals, zinc is most convenient and iron is the classic choice. Dilute HCl is generally used, although dil. $H_2SO_4$ may also be used. But, if the $H_2SO_4$ to be used is too concentrated, the hydrogen evolved from it may be easily contaminated with $SO_2$ and $H_2S$. Nitric acid is not used due to the fact that the nascent hydrogen formed reduces the $HNO_3$ (an oxidising agent) to the oxides of nitrogen, and is itself oxidised to water. Very dilute (about 2%) $HNO_3$, however, reacts with magnesium and manganese to produce hydrogen.

Pure zinc reacts very slowly with dilute acids to produce hydrogen. Commercial zinc is, therefore, used for the purpose. If pure zinc is used, a small amount of copper sulphate solution should be added to the system, when the liberation of hydrogen becomes rapid.

When $CuSO_4$ solution is added to the system, metallic copper deposits at some places on the surface of the zinc metal which goes into solution. This forms galvanic couples between Zn and Cu on the surface of zinc. By the action of acid, those portions of the zinc which are not covered with copper, go into solution, while hydrogen is liberated on the copper. By a process of charge transfer within the metal, *local currents* come into operation (Fig. 9.3).

In the absence of copper (or any other impurity that can form such galvanic couples), the hydrogen can be discharged only at the zinc surface. It is assumed that gaseous hydrogen evolved at the zinc surface remains adherent to the surface as an exceedingly thin film which obstructs the passage of further portions of the zinc into solution. Further liberation of $H_2$ is thereby inhibited, so that the gas bubbles ($H_2$) cannot grow and dislodge. In view of the high overvoltage which is established before $H_2$ can be evolved from the zinc surface, it is likely that the $H^+$ ions cannot be discharged, or at least that the combination of the H atoms to $H_2$ molecules cannot take place on an absolutely pure zinc surface. The effect is so pronounced that very pure zinc is practically insoluble in dil. acids.

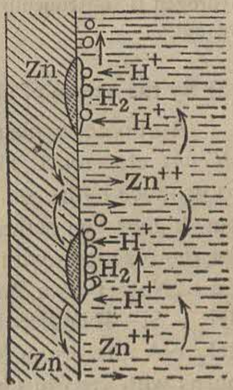


Fig. 9.3

(Conc. HCl may be used for the preparation of hydrogen from Zn, Fe, Al and Sn. It may be mentioned that iron and tin give the *ferrous* and the *stannous* salts respectively due to the reducing action of hydrogen.)

The rate of evolution of hydrogen by the action of dilute acid on a particular metal depends upon the *strength* of the acid. (The term *strength* should not be confused with the concentration of the acid used.) Thus, with the same amount of Zn and the same volume of (N) acid solutions, the rate of evolution of $H_2$ is greater for HCl or $H_2SO_4$ (*strong* acids) than for acetic acid (*weak* acid). Zn liberates $H_2$ from HCl more readily than from $H_2SO_4$.

For the ready and intermittent supply of hydrogen in the laboratory, hydrogen is generally prepared in Kipp's apparatus. Hydrogen obtained from the action of dil. $H_2SO_4$ on commercial zinc is not very pure. It contains many impurities such as arsine ($AsH_3$), phosphine ($PH_3$), hydrogen sulphide ($H_2S$), $CO_2$, $SO_2$, oxides of nitrogen, along with $O_2$ $N_2$, and moisture. The gas may be purified by passing through a train of U-tubes containing the following absorbents to remove the impurities mentioned against each of them :

(*a*) Lead nitrate solution—to remove $H_2S$ ;
(*b*) Silver sulphate solution—to remove $AsH_3$ and $PH_3$ ;
(*c*) Strong KOH solution—to remove $SO_2$, $CO_2$ and the oxides of nitrogen ;
(*d*) Chromous chloride solution—to remove $O_2$, and
(*e*) Solid $P_2O_5$ to remove moisture.

Nitrogen contained in the gas cannot be easily removed. The best way to obtain $H_2$ free from $N_2$ is to pass the gas through a globe containing spongy palladium metal, when $H_2$ is absorbed. $N_2$ is pumped out from the globe. Pure hydrogen is subsequently recovered by heating the globe, and it is collected over mercury.

(h) **By the action of alkali on metal** :

Amphoteric metals like zinc, aluminium, lead, silicon (as *ferro-silicon*) etc. react with strong solutions (20-30%) of caustic alkali to produce hydrogen. Zinc generally reacts at ordinary temperatures, but higher temperatures (boiling with alkali solutions) are needed for the reactions with the other metals.
$Zn+2NaOH=Na_2ZnO_2+H_2$ ; $2Al+2NaOH+2H_2O=2NaAlO_2+3H_2$ ; $Si+4NaOH=Na_4SiO_4+2H_2$ ; $Si+2NaOH+H_2O=Na_2SiO_3+2H_2$. A mixture of ferro-silicon and soda-lime, known as *hydrogenite*, burns with vigorous evolution of hydrogen when ignited.

$Si+Ca(OH)_2+2NaOH=Na_2SiO_3+CaO+2H_2$.

(i) **From hydrocarbons** : Hydrocarbons now-a-days provide a major share of manufactured hydrogen. The cracking of hydrocarbons thermally, in presence of suitable catalysts, produces much hydrogen. Methane, from natural gas, may also be thermally decomposed, but the reaction with steam at 1100°C in presence of a catalyst is generally preferred. The reaction is *endothermic* and the heat is provided by allowing some of the methane to burn in air. $CH_4+H_2O$ (vapour) $=CO+3H_2-48.9$ Kcals. The product is purified as for *water gas*.

(j) **From Coke-oven gas** : Hydrogen is the principal constituent of coke-oven gas (55% $H_2$, 25% $CH_4$, 2% heavier hydrocarbons, 4-6%

CO, 2% and $CO_2$ 10-12% $N_2$). By fractional liquefaction, hydrogen may be commercially obtained from coke-oven gas. The desulphurised coke-oven gas is freed from oxides of carbon by washing with water and sodium hydroxide under pressure. The other impurities are then removed by progressive condensation, leaving hydrogen, which can be freed from the last impurities by cooling in liquid nitrogen.

**PROPERTIES : Physical properties.**—Hydrogen is a colourless gas without taste or smell and it burns with a bluish, very hot flame when ignited in air. It is the lightest of all gases and is virtually insoluble in water. Its thermal conductivity is about 7 times that of air. It can be liquefied to a very light colourless liquid by allowing highly compressed gas below $-240°C$ to flow through a small aperture into vacuum. On evaporating under reduced pressure, liquid hydrogen freezes to a colourless crystalline solid.

At ordinary temperatures, gaseous hydrogen is absorbed by many metals such as palladium, platinum, iron, cobalt *etc.*, of which palladium has the greatest capacity of absorbing of about 800 times its own volume of the gas. The phenomenon is known as the **occlusion of hydrogen**. Finely divided metals occlude hydrogen more effectively. Occlusion of hydrogen decreases with rise of temperature. The occluded gas is given off on heating, and this provides a method of purifying hydrogen. Different views regarding the cause of occlusion of hydrogen by metals like palladium have been proposed from time to time. It has been proposed by some scientists that occlusion takes place due to the formation of certain hydrides like $Pd_2H$, $Pd_3H$, $Pd_4H$ *etc.* The recent view regarding the phenomenon relates it to the formation of *interstitial compounds* in which the hydrogen atoms occupy the holes in the crystal-lattice of palladium metal. This results in the expansion of the metal-lattice in all the three dimensions to fit the hydrogen atoms in the interstitial spaces. The lowering of the density of palladium metal with occluded hydrogen seems to support this view.

The important physical properties of hydrogen is tabulated below :

Density (gm./litre) at 0°C and 760 mm. pressure = 0.08987 gms.
Boiling point $= -252.8°C = 20.4°K$
Melting point $= -257.3°C = 15.9°K$
Critical temperature $= -239.9°C$
Solubility in water at 0°C = 21.5 ml./litre
1st ionization potential = 13.54 volts
Electron affinity = 0.715 e.v.

**Chemical properties.**—Molecular hydrogen is not very reactive chemically at ordinary temperatures due to the highly endothermic nature of the dissociation of $H_2$ molecules. The whole chemistry of hydrogen depends on three distinct electronic processes which are enumerated below :

(i) The loss of the $1s$ electron to form the hydrogen ion, $H^+$, or a proton, which, however, invariably exists in aqueous solution as the $H_3O^+$ (hydroxonium or hydronium) ion, (ii) acquisition of an electron to attain the $1s^2$, configuration of He and thus forming a uninegative hydride ion, $H^-$, as in NaH, KH, $CaH_2$ *etc.*, and (iii) formation of an electron-pair bond by sharing an electron with another atom and thus attaining the $1s^2$ structure again. The bond may be homopolar as in $H_2$ molecules, or heteropolar as in HCl molecule. The absence of any shielding of the nuclear charge by the electron shells in a proton also endows it with certain unique properties such as the formation of *hydrogen bond* (as in water and hydrofluoric acid *etc.*), *hydrogen bridge bond* (as in dioborane), *complex hydrides* (such as $NaBH_4$, $LiAlH_4$ *etc.*). The chemical reactions of molecular hydrogen are summarised below :

Hydrogen gas directly combines with halogens when illuminated by sunlight, (the reaction with iodine requiring the presence of a catalyst: $H_2+X_2=HX$ (X=F, Cl, Br, I). Combination with oxygen is highly exothermic and it requires ignition of mixture of the gases: $2H_2+O_2=2H_2O$. At elevated temperatures ($\sim$500°C) and high pressures (200 atmospheres), it combines with $N_2$ in the presence of a suitable catalyst to give ammonia: $N_2+3H_2 \rightleftharpoons 2NH_3$, the reaction being reversible and exothermic. With most of the other non-metals, it forms hydrides. With certain strongly electropositive metals, it forms salt-like hydrides at somewhat elevated temperatures: $2M+xH_2 \rightarrow 2MH_x$, where M= Na, K, Li, Ca *etc.* At elevated temperatures, it reduces many metallic oxides (other than the oxides of strongly electropositive metals) to lower oxides or to the metal: $M_xO_y+yH_2 \xrightarrow{\text{heat}}$ lower oxides $\rightarrow xM+yH_2O$. In presence of catalyst like Pt, Ni etc., it reduces many organic compounds. In such reactions, aldehydes are reduced to alcohols, nitrogenous organic compounds to ammonia or amines, unsaturated compounds to the saturated ones. The last reaction is utilised to prepare semi-solid or solid fats from liquid oils (as in *Vanaspati* manufacture). Hydrogen combines with carbon monoxide in presence of catalysts to give hydrocarbons or alcohols, the products of the reactions being dependent on the catalyst used.

**Nascent hydrogen** : When hydrogen gas is bubbled through a solution of ferric chloride, the latter is not reduced. But, if ferric chloride solution is added to a mixture of zinc and sulphuric acid (which is evolving hydrogen), the ferric salt is readily reduced to the ferrous state: $FeCl_3+H=FeCl_2+HCl$. Such an activity of hydrogen in the latter case is attributed to a special form of hydrogen which is known as *nascent* (new-born) hydrogen, *i.e.* the hydrogen at the moment of its birth. It is generally supposed to consist of atoms of hydrogen which had no time to join up to form molecules before interaction occurs. Hydrogen liberated at the cathode during electrolysis is also endowed with similar reducing properties.

The above simple reason of the enhanced activity of nascent hydrogen cannot be maintained due to the fact that nascent hydrogen from different sources has different reducing power. A chlorate can be reduced to a chloride by the nascent hydrogen liberated by the action of zinc on dilute sulphuric acid, but it cannot be reduced by the nascent hydrogen formed by the action of water on sodium amalgam. Similarly, if an acidified solution of ferric chloride is treated with equivalent quantities of different metals, the amount of reduction to the ferrous state is different. Again, with electrolytically produced hydrogen, the reducing power depends upon the nature of the cathode used. Such differences are explained by recognising that chemical changes which liberate hydrogen proceed with the liberation of different amounts of energy. The energy available in a particular process may or may not be sufficient to bring about a particular reduction.

Another explanation which has been put forward for the enhanced activity of nascent hydrogen relates it with the size of the bubbles of hydrogen produced. The smaller the bubbles of the gas, the greater is the pressure of hydrogen inside the bubbles, and consequently, greater is the reducing power.

**Atomic hydrogen.**—The energy of dissociation of the hydrogen molecule is 103 Kcals./mole. So, it is possible for the gas to be dissociated into atoms by heat. Atomic hydrogen, is not the same as *nascent* hydrogen. It is formed when hydrogen gas is passed over heated tungsten or platinum wires (2000°C) at a very low pressure (below 0.01 mm.), or when the gas under a very low pressure is subjected to electric discharge in a long tube. The irradiation of a mixture of hydrogen and mercury vapour with mercury resonance radiation of wavelength 2537Å also produces atomic hydrogen. Once produced under such conditions, the atoms of hydrogen do not readily re-unite, thus allowing time to study their reactions. Atomic hydrogen is best generated for studying its chemical reactions in the following way: Hydrogen gas at a very low pressure ($\sim$1 mm. of Hg) is pumped through an electric discharge, the energy of which dissociates $H_2$ molecules. (The formation of hydrogen atoms can be readily detected from the presence of the lines of the Balmer spectrum of hydrogen in the light emitted by the discharge.) The hydrogen atoms, thus formed, cannot re-unite to form $H_2$ molecules because of the fact that the resulting molecule has an energy-content sufficient to cause its dissociation. The re-union of the H-atoms by collision is also prevented by the very low pressure of the gas and the wide tube employed. The gas coming out from the discharge contains appreciable concentration of atomic hydrogen, which decrease with increase of the distance of gas-stream from the discharge zone. Atomic hydrogen is chemically very active. It reacts with certain metals and non-metals at room temperature, to form the corresponding hydrides. It reduces carbon monoxide to formaldehyde : $CO+2H=HCHO$. Many metallic oxides are reduced to metals by atomic hydrogen and many salts are also partially or completely reduced. It also reacts with molecular oxygen to form hydrogen peroxide : $O_2+2H=H_2O_2$. Many metals (e.g. Platinum) catalyse the re-combination of atomic hydrogen to $H_2$.

Atomic hydrogen is used for welding purposes. When a stream of hydrogen gas is blown through a tungsten arc (temperature about 4000°K), about 60% of the molecules are dissociated into atoms. The issuing gas is then allowed to impinge upon the surfaces to be welded. Intense local heating is developed by the re-combination of the atoms on the metal surface, which melts and welds the metal-surfaces and also protects them from oxidation by creating a hydrogen atmosphere.

**Isotopes of Hydrogen** : Hydrogen has three isotopes, *viz.* ordinary hydrogen (${}_1H^1$), heavy hydrogen or **deuterium** (${}_1H^2$ or D) and **tritium** (${}_1H^3$ or T), the relative abundances of the three species being, ${}_1H^1=99.9844\%$, $D=0.0156\%$, T=traces. In their atomic structures, the three isotopes differ only in the composition of their nuclei, in that the nucleus of ordinary hydrogen contains only one proton, while those of deuterium and tritium contain in addition 1 and 2 neutrons respectively, the atomic nucleus in each case being surrounded by a single electron rotating in the 1*s* orbit.

The minute discrepancy in the values of the atomic weights of hydrogen, as determined mass spectrographically and by accurate chemical methods, led Birge to suggest (1931) the existence of a heavier isotope of hydrogen in very small quantities in ordinary hydrogen. Accordingly, Urey subjected a quantity of liquid hydrogen to distillation and obtained a residue whose atomic spectra suggested the presence of a species of double the atomic mass of ordinary hydrogen. Shortly afterwards, Washburn and Urey found that the heavy isotope enriched rapidly in prolonged electrolysis of water, and G.N. Lewis and

MacDonald obtained a few millilitres of pure heavy water, the oxide of the heavier isotope of hydrogen, in 1933.

**Deuterium :**

Gaseous deuterium is prepared by decomposing heavy water (which is available now commercially through long-continued electrolysis of water—see latter in the section of **heavy water**) with sodium, red-hot iron or tungsten, or by the electrolysis of a solution of anhydrous $Na_2CO_3$ in heavy water. It may also be prepared by the diffusion of gaseous hydrogen, or the distillation of liquid hydrogen, but these methods are far more troublesome than the first method.

Deuterium and its compounds are obtainable in appreciable quantities and as such, their properties have been studied in more details than those of tritium. The important physical properties of deuterium are given below along with those of ordinary hydrogen :

| | $D_2$ | $H_2$ |
|---|---|---|
| Molecular weight | 4.02838 | 2.01574 |
| Boiling point (°K) | 23.6 | 20.38 |
| Melting point (°K) | 18.63 | 13.95 |
| Vapour pressure at the m.p. (m.m.) | 121.0 | 54 |
| Heat of dissociation (cals./mole) | 104.5 | 102.5 |
| Latent heat of evaporation (cals./mole) | 302.2 | 219.7 |

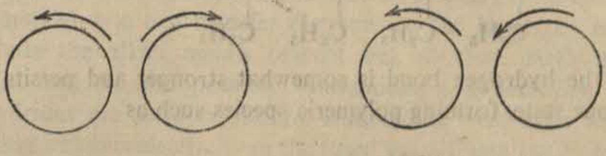
The **chemical properties** of deuterium are more or less identical with those of hydrogen, but the heavier isotope reacts somewhat slowly and less completely than the lighter isotope. Thus, the reactions of hydrogen with $N_2O$ or oxygen are about twice as fast as those with deuterium. Deuterium reacts directly with halogens ($Cl_2$, $Br_2$, $I_2$) to form the deuterium halides : $D_2+Cl_2=2DCl$ ; deuterium fluoride is formed by the interaction between AgF and $D_2$ at 110°C : $2AgF+D_2=2Ag+2DF$. Deuterium undergoes some *exchange-reactions* in which the light isotope is replaced by the heavier one : $H_2+D_2 \rightleftharpoons 2HD$ ; $D_2+H_2O \rightleftharpoons D_2O+H_2$ ; $3D_2+C_6H_6 \rightleftharpoons C_6D_6+3H_2$. Deuterium is used in the study of mechanisms of chemical reactions. Deuteron (${}_1D^2$) is used as a projectile in artificial transmutation of elements.

**Tritium :**

The third isotope of hydrogen (${}_1T^3$) was discovered (1934) as a product of the bombardment of deuterium compounds with fast deuterons (${}_1D^2+{}_1D^2 \rightarrow {}_1T^3+n$). It is most conveniently prepared through the irradiation of lithium or its compounds with slow neutrons in a nuclear reactor : ${}_3Li^6+n \rightarrow {}_2He^4+{}_1T^3$. The isotope, thus produced, may be oxidised to $T_2O$ and isolated in this form, or it may be adsorbed in uranium metal as $UT_3$ and subsequently regenerated by heating at 500°C. By either of the above processes, tritium is separated from helium. Small amounts of tritium are formed in the uppermost region of the atmosphere, probably as a result of the reaction, ${}_7N^{14}+n \rightarrow {}_6C^{12}+{}_1T^3$, the neutron being available from outer space.

Tritium is a radioactive isotope which decays by the emission of low energy $\beta$-particles, the half-life being 12.4 years. The product of the decay is the helium isotope, ${}_2He^3$. The boiling point of tritium is 25.04°K. It is used in tracer experiments.

**Allotropes of Hydrogen : Ortho- and para-hydrogen.**—A molecule of hydrogen consists of two hydrogen atoms. Due to the nuclear spin of the hydrogen atoms, it was predicted by Heisenberg and Hund (1927) that two types of hydrogen molecules should be available—the one having the spins of the two nuclei *parallel* or *aligned*, and the other having their spins *anti-parallel* or *opposed*. Such modifications of substances are not a speciality for a hydrogen molecule alone, but they should also be found in other symmetrical molecules like $D_2$, $N_2$, $F_2$, $Cl_2$ *etc.*, whose nuclei have spin momenta. But, among all these molecules, only hydrogen and deuterium have substantial differences in the physical properties of the two forms. The low specific heat of hydrogen at the boiling temperature of liquid air and the alterations in intensity in the band spectrum of molecular hydrogen at low temperatures (Mecke, 1924) also suggested the existence of two modifications of molecular hydrogen. In 1929, K.F. Bonhoeffer and P. Hartick succeeded in isolating in pure form, one of the two allotropes by the adsorption of ordinary hydrogen on wood charcoal at about 20°K. This was termed *para-hydrogen* and has opposite nuclear spins. The variety with parallel nuclear spins has been designated as the *ortho-hydrogen*, although it could not be isolated in the pure state. Ordinary hydrogen consists of 3 parts of *ortho-hydrogen* with one part *para-hydrogen*. There are considerable differences between the physical properties (*e.g.* boiling points, specific heats, thermal conductivities) of the two varieties, and these arise because of the differences in their internal energy. The symmetrical *para*-form has the lower internal energy than the ortho form. The equilibrium mixture of the two forms at absolute zero temperature contains 100% of the *para*-form. With the rise of temperature, the proportion of the *ortho*-form increases upto a limiting value of 75%. *Para*-hydrogen is prepared by the adsorption of ordinary hydrogen in charcoal at the liquid air temperature. It can be kept for weeks at room temperature in a glass vessel, because the ortho-para conversion is very slow in the absence of catalysts (such as atomic hydrogen, Fe, Ni, Pt, W and other paramagnetic substances or ions). *Para*-hydrogen has a rather higher vapour pressure and slightly lower boiling and melting points than ordinary hydrogen. The

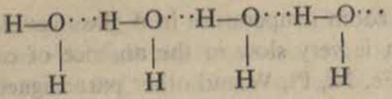


[The circles represent hydrogen nuclei.]

Fig. 9.4

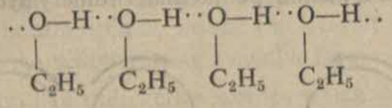
heat of transformation from the ordinary hydrogen to *para*-hydrogen is 0.337 Kcal. per mole at absolute zero. As the pure *ortho*-hydrogen could not be isolated, its properties were known by extrapolation methods. The thermal conductivities and the heat capacities of the two forms of hydrogen are different. The magnetic moment of *para* hydrogen is zero (because the opposite nuclear spins compensate) ; but, for *ortho* hydrogen, the magnetic moment (extrapolated from data for known ortho-para mixtures) approximates to twice the moment of a proton. *Ortho-* and *para*-hydrogen are, however, chemically identical.

**Hydrogen Bond.**—Once a hydrogen atom has formed a covalent bond with another element, the hydrogen nucleus is relatively unshielded on the side remote from that bond. If the bond is strongly dipolar, which is the case if the hydrogen atom is bonded to an electronegative element such as fluorine, oxygen or nitrogen, the positive end of the dipole may be expected to interact particularly strongly with other covalently saturated electronegative atoms, again such as fluorine, oxygen or nitrogen. This suggests the formation of bonds of the general type, $-\overset{\delta-}{X}——\overset{\delta+}{H}\ldots\ldots\overset{\delta-}{X}-$, with a strength intermediate between ordinary Van der Waals force and normal chemical bonds. Such a bond is called a **hydrogen bond** (for details, see chapter III). The formation of hydrogen bonds in compounds is corroborated by spectroscopic evidences. In liquid water, the hydrogen atom forms a bridge between two oxygen atoms, resulting in the association of $H_2O$ molecules, which is responsible for the relatively higher boiling point of water (*cf.* the lower b.p.'s of $H_2S$, $H_2Te$, $NH_3$ *etc.*).



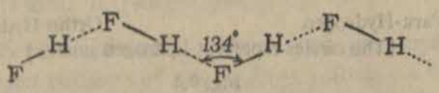
$$\mathrm{H{-}\underset{\underset{H}{|}}{O}\cdots H{-}\underset{\underset{H}{|}}{O}\cdots H{-}\underset{\underset{H}{|}}{O}\cdots H{-}\underset{\underset{H}{|}}{O}\cdots}$$

Ethyl alcohol is similarly associated, which also explains its liquid state.

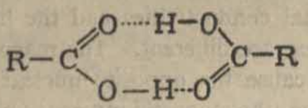


$$\mathrm{..\underset{\underset{C_2H_5}{|}}{O}{-}H\cdots\underset{\underset{C_2H_5}{|}}{O}{-}H\cdots\underset{\underset{C_2H_5}{|}}{O}{-}H\cdots\underset{\underset{C_2H_5}{|}}{O}{-}H..}$$

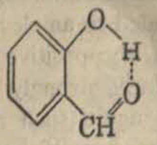
In HF, the hydrogen bond is somewhat stronger and persits even in the vapour state, forming polymeric species such as



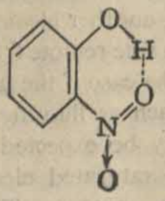
Hydrogen bonding occurs also in many organic compounds such as acetic acid which exists as dimers.



Such bonding is also possible within a molecule of a compound, such as in salicylaldehyde, *o*-nitrophenol *etc.*, affecting their solubilities in water.



SALICYLALDEHYDE



*o*-nitrophenol

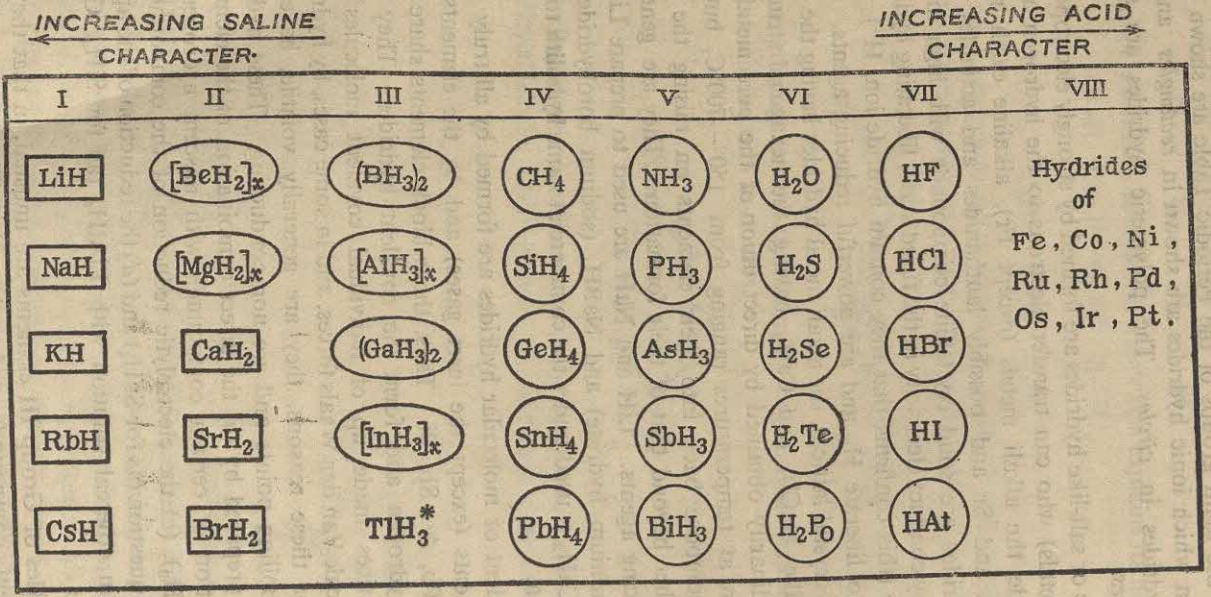
**HYDRIDES :** Binary compounds of the elements with hydrogen are called the hydrides. Various elements form hydrides with divergent properties and types of bonding which depend mainly on the electronegativities of the elements combined with hydrogen. All the known hydrides have been divided into three fairly distinct classes, *viz.* (i) *ionic* or *salt-like* (*saline*) hydrides, (ii) *covalent* or *molecular* hydrides and (iii) *metallic* or *interstitial* hydrides. Another type of hydrides is often recognised as the *polymeric* hydrides, but they are actually special cases of covalent or molecular hydrides. The hydrides formed by the elements of the main groups of the Periodic Table are shown in the Table 9.1, in which ionic hydrides are shown in *rectangles* and the covalent hydrides in *circles*. The polymeric hydrides are shown within *ellipses*.

(i) Ionic or salt-like hydrides are formed by strongly electropositive elements (metals) who can transfer electrons to the hydrogen atoms. These include the alkali metals (except Fr), alkaline earth metals like Ca, Ba and Sr and possibly lanthanides and actinides. The salt-like hydrides are solid crystalline compounds with high melting points. They conduct electricity in the fused state, liberating hydrogen at the anode (this confirms that they contain hydride ion, $H^-$), react with water to liberate $H_2$ and are powerful reducing agents. They possess ionic crystal lattices, the alkali metal hydrides having the cubic structures (like NaCl), and $CaH_2$ having the hexagonal structure. They are ordinarily obtained by direct union of the pure metal and dry hydrogen at temperatures ranging from 150°—700°C, but the hydrides decompose back into their elements on raising the temperature further beyond that of their formation. They are generally used as reducing agents. LiH and NaH are used to prepare $LiAlH_4$ (lithium aluminium hydride) and $NaBH_4$ (sodium borohydride) respectively. $CaH_2$ is used under the commercial name **hydrolith** to produce hydrogen.

(ii) Covalent or molecular hydrides are formed by all truly nonmetallic elements (except the inert gases) and by the elements like Al, Ga, Sn, Pb, As, Sb, Bi. Thus, the *p*-block elements share electrons with hydrogen and form the covalent hydrides. They have molecular lattices made up of individual covalent molecules held together by weak Van der Waals forces, and in some cases, by hydrogen bonding. For these reasons, they are generally volatile, have low melting and boiling points and are non-conducting. These hydrides are generally prepared by (*a*) the direct combination of the elements, (*b*) the reduction of certain compounds with nascent hydrogen (as for $AsH_3$, $SbH_3$), (*c*) the electrolytic reduction of the compounds of the element in question (as for $SnH_4$) and (*d*) the reduction of the appropriate halide in ethereal solution with $LiAlH_4$ (as for $SiH_4$, $GeH_4$, $SnH_4$ *etc.*).

The hydrides of Group III elements are unusual, in that they are electron-deficient compounds and polymeric. The simplest boron hydride is $B_2H_6$, and aluminium hydride is $(AlH_3)_x$, (*x* is not difinitely known). Except the halogens, many of the elements forming covalent

TABLE 9.1


INCREASING SALINE CHARACTER
INCREASING ACID CHARACTER

| I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|
| LiH | $[BeH_2]_x$ | $(BH_3)_2$ | $CH_4$ | $NH_3$ | $H_2O$ | HF | Hydrides of Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt. |
| NaH | $[MgH_2]_x$ | $[AlH_3]_x$ | $SiH_4$ | $PH_3$ | $H_2S$ | HCl | |
| KH | $CaH_2$ | $(GaH_3)_2$ | $GeH_4$ | $AsH_3$ | $H_2Se$ | HBr | |
| RbH | $SrH_2$ | $[InH_3]_x$ | $SnH_4$ | $SbH_3$ | $H_2Te$ | HI | |
| CsH | $BrH_2$ | $TlH_3^*$ | $PbH_4$ | $BiH_3$ | $H_2P_o$ | HAt | |

1. Hydrides enclosed in rectangles are ionic or salt-like hydrides.
2. Hydrides enclosed in circles are covalent hydrides.
3. Hydrides enclosed in ellipses are polymeric or polynuclear hydrides.
4. Group VIII |hydrides are interstitial hydrides.

* Known only as double compounds, such as $TlH_3.3GaH_3$.

hydrides are known to form polynuclear hydrides in which two or more of the atoms of these elements are directly bonded to each other. This tendency is at maximum with carbon. Most of the polymeric hydrides are solids and conductors of electricity.

(iii) Metallic or Interstitial hydrides : The *d*-block (transition) elements and Be and Mg (of *s*-block) form metallic hydrides, if they react with hydrogen at all. Hydrogen gas is often absorbed reversibly by these metals (the tendency being maximum for palladium), forming the so-called hydrides, which are less dense than the parent metals. The chemical composition of the products of such changes is variable, *i.e.* they are non-stoichiometric. In most cases, the *hydrides* have properties quite similar to those of the metal itself. In many cases, the formation of such hydrides results in no fundamental changes in the metal lattice. There seems to be every evidence that in such cases, hydrogen, which enters the metal lattice, is occupying holes (interstices) between the metal atoms (or ions) and is thus held in solid solution. The strongly reducing properties of these hydrides suggest that the hydrogen is present in the atomic state. Many of these hydrides are conductors of electricity and some are semi-conductors.

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## WATER

*Formula* : $H_2O$ *Molecular weight* = 18

*Water was shown to be a compound (and not an element) by Cavendish* (1781)

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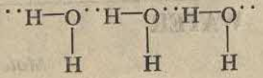
**OCCURRENCE** : Water occurs abundantly in nature. In the liquid form it occurs in oceans, rivers, springs and wells ; in the solid state (ice), on some mountain peaks and in arctic regions. Small quantities of water vapour are present in the atmosphere. Animal and vegetable tissues contain large quantities of water. As *water of crystallisation* or *lattice water*, it occurs in many rocks and minerals.

Different types of natural water : (a) **Sea water** contains maximum amount of dissolved salts (about 2.6% sodium chloride and 1% other salts). It is *hard* and unsuitable for drinking purpose. (b) **River water.**—While flowing over the surfaces of mountains and earth, river water collects suspended impurities like clay particles and many dissolved impurities like salts of calcium, magnesium, iron, sodium and potassium. River water is *hard*, but it can be used for drinking purposes, provided it is not contaminated with other harmful matter. (c) In **Well and Spring water,** the suspended impurities are absent due to filtration through porous strata of earth. But, the dissolved metal-salts are present in larger amounts in them. Water from these sources are also *hard.* (d) **Mineral water.**—In addition to the common dissolved salts, this water contains sulphuretted hydrogen, ferrous salts and dissolved gases like helium and traces of radium emanation. This water is also classed as *hard* water. (e) **Rain water.**—This is the purest natural water and is typically *soft*. Small quantities of some dissolved atmospheric gases like oxygen, nitrogen and carbon dioxide, together with suspended dust particles from the air, are present in it. Rain water may also contain traces of ammonium nitrate and nitric acid produced during thunderstorm and also very small amounts of sulphurous and sulphuric acids from sulphur dioxide formed by the burning of coal which contains iron pyrites ($FeS_2$).

**PROPERTIES : Physical properties.**—Pure water is a colourless liquid without any taste or smell. It freezes at 0°C and boils at 100°C under normal atmospheric pressure. It has a maximum density of unity (1gm./ml.) at 4°C. Its density in the solid state (ice) is 0.92 and so, ice floats on water. It is practically a non-conductor of electricity due to its negligible ionisation into hydrogen and hydroxyl ions, and also a bad conductor of heat.

Water is present in many crystalline hydrates of definite composition, *e.g.* $CuSO_4 . 5H_2O$ (*Blue vitriol*) ; $Na_2SO_4 . 10H_2O$ (*Glauber's salt*) ; $FeSO_4 . 7H_2O$ (*Green vitriol*), $C_2H_2O_4 . 2H_2O$ (*Oxalic acid dihydrate*).

In the liquid state, the water molecules are *associated* through hydrogen bonding, giving rise to polymeric chain of the type $(H_2O)_n$, as shown below :



$$\cdot\cdot\mathrm{H}-\underset{\substack{|\\ \mathrm{H}}}{\mathrm{O}}\cdot\cdot\mathrm{H}-\underset{\substack{|\\ \mathrm{H}}}{\mathrm{O}}\cdot\cdot\mathrm{H}-\underset{\substack{|\\ \mathrm{H}}}{\mathrm{O}}\cdot\cdot$$

Such a structure is supported by various physical and chemical evidences, and it offers explanation for certain *abnormal* properties of water, *viz.* high density, high melting and boiling points, high specific heat *etc.*, as compared with those of $H_2S$, $H_2Se$ and $H_2Te$.

**Water as a solvent.**—Water behaves as a good ionising solvent due to its high dielectric constant (81), and it readily dissolves ionic compounds like acids, bases and salts, the resultant solutions being good conductors of electricity. Water actually behaves as an *amphiprotic* solvent, acting both as a proton-acceptor (base) and a proton-donor (*acid*) : $CH_2COOH + H_2O \rightleftharpoons CH_3COO^+ + H_3O^+$ ;
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$.

**Absorption of water by dehydrating agents.**—Water is absorbed by many substances like conc. $H_2SO_4$, fused $CaCl_2$, $P_2O_5$, CaO (quicklime), magnesium perchlorate, silica gel and anhydrous $Na_2SO_4$. Absorption of water by desiccants is mainly a physical process ; but, with some desiccants, chemical reaction takes place, as is the case with $P_2O_5$ [$P_2O_5 + 3H_2O = 2H_3PO_4$].

**Chemical properties.**—Water takes part in a variety of chemical reactions.

(i) **Reactions with metals.**—Many metals and amalgams react with water at different temperatures to form hydrogen and the hydroxides (or oxides) of the metals concerned. [For the details of these reactions, the preparation of hydrogen from water in the previous section may be seen.]

(ii) **Reactions with non-metals.**—Non-metals like carbon and sulphur react with steam at high temperatures. A mixture of carbon monoxide and hydrogen (*water-gas*) is obtained on passing steam over white-hot carbon : $C+H_2O=CO+H_2$. When steam is passed through boiling sulphur, small amounts of $SO_2$ and $H_2$ are formed : $S+2H_2O \rightleftharpoons SO_2+2H_2$.

(iii) **Reactions with metallic and non-metallic oxides.**—Many metallic oxides (which are in most cases *basic oxides*) react with water, either in the cold or on boiling, to form the corresponding metal hydroxides : $Na_2O+H_2O=2NaOH$ ; $CaO+H_2O=Ca(OH)_2$ ; $MgO+H_2O=Mg(OH)_2$. The non-metallic oxides (*acidic oxides*) react with water to produce the corresponding acids : $CO_2+H_2O=H_2CO_3$ ; $SO_2+H_2O=H_2SO_3$ ; $P_2O_5+3H_2O=2H_3PO_4$ ; $N_2O_5+H_2O=2HNO_3$.

(iv) **Hydrolytic decomposition by water.**—Many inorganic and organic compounds suffer hydrolytic decomposition with water. Compounds like metallic nitrides, phosphides, carbides, hydrides *etc.* are decomposed by water to form the corresponding metallic hydroxides, with the liberation of ammonia, phosphine, acetylene, hydrogen *etc.* respectively.

$AlN+3H_2O=Al(OH)_3+NH_3$ ; $Ca_3P_2+6H_2O=3Ca(OH)_2+2PH_3$ ;
$CaC_2+2H_2O=Ca(OH)_2+C_2H_2$ ; $CaH_2+2H_2O=Ca(OH)_2+2H_2$.

Certain metallic salts and organic compounds are readily hydrolysed by water : $FeCl_3+3H_2O \rightleftharpoons Fe(OH)_3+3HCl$ ;

$$\underset{\text{(acetyl chloride)}}{CH_3COCl} + H_2O \rightleftharpoons \underset{\text{(acetic acid)}}{CH_3COOH} + HCl.$$

$$PCl_5+H_2O=POCl_3+2HCl.$$

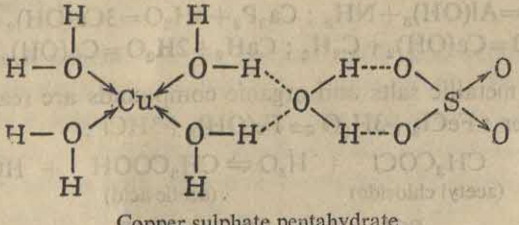
(v) **Decomposition of water.**—Steam is decomposed into hydrogen and oxygen by electric sparking, or in contact with hot platinum wire at about 2000°C. As already shown, water can be decomposed by electrolysis and by the action of certain metals on it. Water is also decomposed by chlorine, either under the influence of sunlight or on passing a mixture of steam and chlorine gas through a strongly heated silica tube, containing broken porcelain pieces :

$$2H_2O+2Cl_2=4HCl+O_2.$$

(vi) **Catalytic action of water.**—Water catalyses certain chemical changes which do not take place when the reacting substances are perfectly dry. Dry carbon monoxide and hydrogen do not burn in dry oxygen ; perfectly dry ammonia and hydrogen chloride do not combine into ammonium chloride ; thermal dissociation of ammonium chloride is retarded by its prolonged drying ; sodium can be melted in dry chlorine without any reaction.

**Water of Crystallisation.**—When crystallised from water, many compounds separate with one or more molecules of the solvent per molecule of the compound. These water molecules are called *water of crystallisation*. The number of such molecules of water depends on the temperature of crystallisation, and the same compound may form more than one hydrate. Copper sulphate crystallises with five molecules of water ($CuSO_4.\ 5H_2O$), ferrous sulphate with seven molecules of water ($FeSO_4.\ 7H_2O$, *green vitriol*), sodium carbonate forms three different hydrates with 10, 7 and 1 molecule of water. The colour of some hydrated salts differs strikingly from that of the corresponding anhydrous salts. $CuSO_4.\ 5H_2O$ is blue in colour, while the anhydrous $CuSO_4$ is practically white ; hydrated cobaltous chloride is pink, while the anhydrous variety is blue.

In many salt hydrates, the water molecules fill up the vacant spaces in the corresponding crystal lattices (*lattice water*) and are bound by the central metal ion by some weak electrostatic force. These are called *lattice water*. As a result, the removal of such water molecules breaks up the crystalline form and sometimes the molecule itself. In some salt-hydrates (like $CuSO_4.\ 5H_2O$ ; $ZnSO_4.\ 7H_2O$), some molecules of water are attached to the sulphate ion by *hydrogen bond* and are thus more tightly bound than the other molecules of water. These are called *anion-water* and they remain attached rather strongly to the parent molecule, and their removal requires heating to higher temperatures.



Copper sulphate pentahydrate

## HARDNESS OF WATER

**Hard and Soft Water.**—Depending upon the behaviour of natural water toward soap, they have been divided into *soft water* and *hard water*.

A sample of water which readily forms *lather* with soap is called *soft water*, and that variety which does not readily produce *lather* with soap is called *hard water*.

**Cause of hardness.**—Hardness of water is due to the presence of soluble (chlorides, sulphates and bicarbonates) salts of calcium, magnesium and iron in it. The chlorides and sulphates of these metals are directly dissolved out by water from soil. The bicarbonates of calcium, magnesium or iron do not occur in earth's surface ; instead, insoluble carbonates like $CaCO_3$, $MgCO_3$ or $FeCO_3$ are found in soil. These insoluble carbonates are transformed into soluble bicarbonates by water which contains some quantity of dissolved atmospheric carbon dioxide. These soluble bicarbonates are taken up by water during its flow, and it becomes hard.

$$CaCO_3+CO_2+H_2O = Ca(HCO_3)_2.$$
$$MgCO_3+CO_2+H_2O = Mg(HCO_3)_2.$$
$$FeCO_3+CO_2+H_2O = Fe(HCO_3)_2.$$

**Reaction of hard water with soap.**—Ordinary soaps are sodium or potassium salts of organic acids like stearic, palmitic or oleic acids. The soluble calcium, magnesium and iron salts of hard water react with soaps, forming the corresponding salts of these organic acids, which being insoluble in water, rise to the surface as a *scum*. Until all the calcium, magnesium or iron compounds are removed, no soap passes into solution and there is no cleaning action, resulting in a great wastage of soap.

$$\underset{\text{(Soluble soap)}}{\text{Sodium stearate}}+\text{Ca-salt}=\underset{\text{(Insoluble scum)}}{\text{Calcium stearate}}\downarrow+\text{Sodium salt.}$$

[The presence of sodium or potassium salts in water, however, does not cause any hardness. The presence of any metallic ion (in water) whose stearate, palmitate or oleate are insoluble in water, makes it hard.]

Hard water is, therefore, unsuitable for laundry purposes for the reason of soap-wastage. Such water is also not suitable for boilers. The use of hard water in boilers results in the deposition of hard, heat-insulating crusts or scales of sulphates or carbonates of calcium and magnesium on the boiler-walls. This causes greater consumption of fuel to heat the boilers and also rapid deterioration of boilers due to over-heating. Hard water is not also suitable in paper and dyeing industries, as also for cooking purposes.

**Classification of hardness of water.**—The hardness of water has been classified as *temporary* and *permanent*.

*Temporary hardness* : This is caused by the presence of bicarbonates of calcium, magnesium or iron in water. This type of hardness can be removed easily by simple boiling, and so, it is termed *temporary hardness*. The soluble bicarbonates of these metals are decomposed into insoluble carbonates (ferric hydroxide, in the case of iron) by heating and they can be removed by filtration.

$$Ca(HCO_3)_2 = CaCO_3 \downarrow + H_2O + CO_2,$$

$$Mg(HCO_3)_2 = MgCO_3 \downarrow + H_2O + CO_2,$$

$$Fe(HCO_3)_2 = FeCO_3 \downarrow + H_2O + CO_2.$$

$$[4FeCO_3 + 6H_2O + O_2 \text{ (air)} = 4Fe(OH)_3 \downarrow + 4CO_2]$$

Temporary hardness can also be removed by the addition of calculated amount of slaked lime (**Clark's process**), by the reaction :

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 \downarrow + 2H_2O.$$

If magnesium bicarbonate is present, double the amount of lime is required to precipitate magnesium hydroxide,

$$Mg(HCO_3)_2 + 2Ca(OH)_2 = 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O.$$

*Permanent hardness* : The chlorides and sulphates of calcium and magnesium give rise to *permanent hardness* in water. [These salts cannot be removed from water by simple boiling.] Softening (*i.e.* the removal of hardness) of permanently hard water can be effected by adding sodium carbonate to it so as to precipitate insoluble $CaCO_3$ and $MgCO_3$ :

$$CaSO_4 + Na_2CO_3 = CaCO_3 \downarrow + Na_2SO_4 ;$$

$$MgCl_2 + Na_2CO_3 = MgCO_3 \downarrow + 2NaCl.$$

[Temporary hard water can also be softened by this method.]

**Softening of hard water.**—On a large scale, hard water is softened by any one of the following processes :

(i) Lime-soda process, (ii) Permutit process,
(iii) Phosphate process, (iv) Ion-exchange process.

**(i) Lime-soda process :** In this process, hard water is treated with a mixture of slaked lime and sodium carbonate (called the *lime-soda mixture*). In solution, the equilibrium, $Na_2CO_3+Ca(OH)_2 \rightleftharpoons CaCO_3+2NaOH$, is attained. The lime-soda mixture thus behaves as a mixture of calcium hydroxide, sodium carbonate and sodium hydroxide. The hardness of water due to calcium salts is removed by the reaction, $CaCl_2+Na_2CO_3 = CaCO_3 \downarrow +2NaCl$, and that due to magnesium salts by, $MgSO_4+2NaOH = Mg(OH)_2+Na_2SO_4$. [A small quantity of sodium aluminate is added to fecilitate the precipitation of finely divided magnesium hydroxide by coagulation, which is enhanced by heating.] The precipitated salts are filtered through filter-beds and soft water is thus obtained.

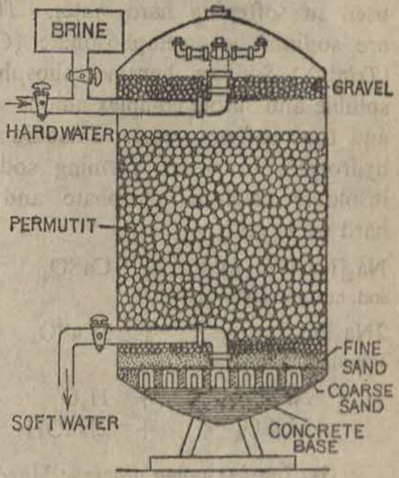


Fig. 9.5—Softening of water : Permutit process.

**(ii) Permutit process :** This is widely used for softening hard water. Hard water is percolated through a column of naturally occurring *zeolites*[*] or artificially prepared sodium aluminio-silicate. When the hard water is passed through zeolite, its sodium ions are replaced by calcium and magnesium ions present in the water. When all the sodium ions of zeolites in the column are thus replaced, the zeolites become *exhausted*.

The passage of the hard water is then stopped and the zeolites are *revived* by passing a strong solution of sodium chloride through the column, when it becomes ready again for softening hard water. The whole process may be represented by the following chemical reactions :

Softening : Sodium-zeolite+Ca-salt=Ca-zeolite+sodium salt
Sodium-zeolite+Mg-salt=Mg-zeolite+sodium salt

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[*] Zeolites are naturally occuring alkali or alkaline earth-metal alumino-silicates, and the sodium derivative is commonly represented by the formula, $Na_2O$, $Al_2O_3$, $4SiO_2$, $2H_2O$. An artificial mixture, resembling zeolites, is prepared by heating a mixture of sand, china clay and an alkali carbonate.

Revival : Ca-zeolite+sodium chloride=sodium-zeolite
+calcium chloride
Mg-zeolite+sodium chloride=sodium-zeolite
+magnesium chloride.

This process is also called *base-exchange* or *zeolite* process.

**(iii) Phosphate process** : Many forms of sodium phosphate are used in softening hard water. The most important among them are sodium hexametaphosphate (*Calgon*) and trisodium phosphate (*Tripsa*). Sodium hexametaphosphate forms non-ionisable, highly soluble and stable complex anions with calcium, magnesium and iron and thus softens water. Trisodium phosphate, on the other hand, hydrolyses in water, forming sodium hydroxide, and precipitates insoluble calcium phosphate and magnesium hydroxide, making hard water soft.

$$\underset{\text{Sod. hexametaphosphate}}{Na_2[Na_4(PO_3)_6]} + CaSO_4 = \underset{\text{Soluble calcium complex}}{Na_2[Na_2Ca(PO_3)_6]} + Na_2SO_4.$$

$$\underset{\text{Trisodium phosphate}}{2Na_3PO_4} + 3CaSO_4 = Ca_3(PO_4)_2 + 3Na_2SO_4.$$

$$Na_3PO_4 + H_2O \rightleftharpoons Na_2HPO_4 + NaOH,$$

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4.$$

**(iv) Ion-exchange process** : Hard water is easily softened, or rather *de-ionised* (or *de-mineralised*) by synthetic *ion-exchange resins*. [By *de-ionised* or *de-mineralised* water is meant a sample of water which contains no dissolved electrolytes.]

Ion-exchange resins or ion-exchangers are insoluble solid materials (generally used in the form of granules) which carry exchangeable cations and anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign, when the ion-exchanger is in contact with an electrolyte solution. Carriers of exchangeable cations are called *cation-exchangers*, and carriers of exchangeable anions are called *anion-exchangers*. A typical cation-exchange reaction is, $2NaX(Solid) + CaCl_2(aq.) \rightleftharpoons CaX_2\ (Solid) + 2NaCl(aq.)$, and a typical anion-exchange reaction is, $2XCl\ (solid) + Na_2SO_4\ (aq.) \rightleftharpoons X_2SO_4\ (Solid) + 2NaCl(aq.)$.

[X represents a structural unit of the ion-exchanger.]

The first process is employed in water-softening, where the calcium (and magnesium) ions of hard water are exchanged by $Na^+$ ions which impart no hardness to water.

Ion-exchangers owe their characteristic properties to a peculiar feature of their structure. They consist of a framework which is held together by chemical bond or lattice energy. This framework carries a positive or negative surplus charge which is compensated by ion of opposite sign, called the *counter-ion*. The counter-ions are free to move within the framework and can be replaced by other ions of the same sign. (Such replacement may be, in some cases, *selective* or *preferential.*)

The framework of a cation-exchanger may be regarded as a macromolecular (or crystalline) polyanion, and that of an anion-exchanger as a similar polycation.

Zeolites used in the permutit process, are *natural ion-exchangers* (naturally occuring alumino-silicates of alkali metals). *Synthetic* alumino-silicates, with completely regular crystal structures, have also been prepared and used under the name *molecular sieves*. These are also typical cation-exchangers. The synthetic organic ion-exchangers or *ion-exchange resins* are the most important class of ion-exchangers and are widely used now-a-days in laboratories and industries. They are typical gel (hydrophobic). Their framework or the so-called *matrix* consists of irregular macromolecular, three-dimensional network of hydrocarbon chains, and is, therefore, cross-linked poly-electrolytes. The matrix carries ionic groups such as, $-SO_3^-$, $-COO^-$, $-PO_3^{-2}$, $-AsO_3^{-2}$ in cation-exchangers, and $-NH_3^+$, $>NH_2^+$, $>N^+<$, $>S^+$, in anion-exchangers. There are hundreds of synthetic ion-exchange resins which are sold in the market under different trade-names, and are used according to the particular necessity. A few typical ion-exchange resins are listed below :

| *Matrix* | *Ionic groups* | *Name* |
|---|---|---|
| 1. **Cation-exchanger** | | |
| *Polystyrene resins* | $-SO_3^-$ | Amberlite IR-120<br>Dowex—50<br>Zeo karb—225 |
| Phenolic resins | ,, | Zeo karb—215 |
| 2. **Anion-exchanger** | | |
| Polystyrene resins | $-NR_3^+$<br>(R=alkyl) | Amberlite IRA—400<br>Dowex—I<br>Dowex—II |

In softening or de-ionising water, both a cation-exchanger and an anion-exchanger are used in succession. The cation-exchanger, which is used, carries $H^+$ as its counter-ion (called the $H^+$-form) and the anion-exchanger carries $OH^-$ as the counter-ion (called the $OH^-$ form). The ion-exchangers are kept in two cylinders and the impure water is allowed to trickle down through the two columns of the exchangers, one after another, as shown schematically in fig. below. During passage through the cation-exchanger, all the metallic cations present in water are exchanged by $H^+$ ions, with the formation of equivalent amount of free acids of the corresponding anions of the metal salts. The water coming out of this column is, therefore, acidic (though completely free from metal ions), and as such is hardly useful for any purpose. [When bicarbonates of metals are only present in the hard water, the resultant $H_2CO_3$ is removed by simply blowing air through the solution (*aeration*), when $H_2CO_3$ is decomposed into $CO_2$

and $H_2O$, and the former is driven out.] The resultant acids are removed on passing this water through the second column containing the anion-exchanger. The anion-exchanger exchanges the anions of the acids (in water) by hydroxyl groups, forming water. The combined effect of the cation- and anion-exchangers, therefore, produces very pure water, practically free from all dissolved electrolytes, and this water is as good as *distilled water.* The chemical reactions that take place in the process may be represented by the following equations, taking a chloride as an example :

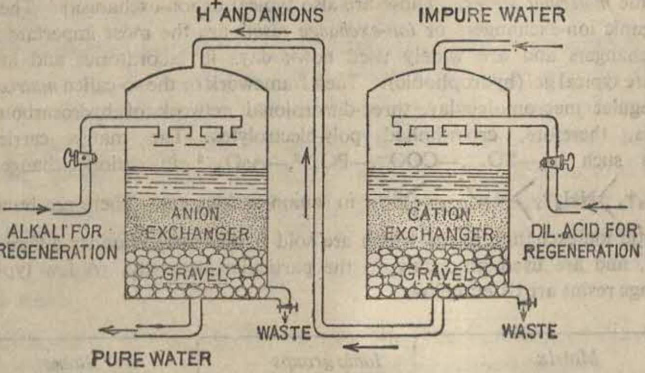


Fig. 9.6—De-ionisation of water using both cation- and anion-exchangers in succession.

Cation-exchange : $MCl_x + xHR = R_xM + xHCl$

(HR represents a cation-exchanger and M=a metal ion.)

Anion-exchange : $HCl + R_3N.OH = R_3N.Cl + H_2O$.

($R_3N.OH$ represents an anion-exchanger.)

As a result of continuing the process for some length of time, the ion-exchangers become *fouled* (*i.e.* loaded with metallic cations and anions, as the case may be), and consequently, cannot carry on the ion-exchange process effectively. They are, then, *re-activated* or *revived* by passing a 0.2M solution of $H_2SO_4$ through the cation-exchanger, and a 0.2M solution of NaOH through the anion-exchanger, and washing with distilled water after such treatment, when the $H^+$-form of the cation-exchanger and the $OH^-$-form of the anion-exchanger are regenerated and are usable again.

Many commercial apparatus are available in the market under the name *De-ioniser* or *De-mineraliser* for preparing de-ionised water. They generally use different synthetic ion-exchange resins for this purpose, the principle of working of the apparatus being the same as described above. The apparatus is generally provided with a meter which directly reads the conductivity values of the outgoing water to ensure effective de-ionisation. When the conductivity values, as recorded in the meter, are high, it is understood that the outgoing water contains dissolved electrolytes (ions); such water is rejected and the apparatus is re-set, after reviving the ion-exchangers and controlling the flow of the impure water through the resins.

**The difference between permutit process and ion-exchange process.**—Each of the two processes softens water through the same mechanism, viz. by exchange of $Ca^{+2}$, $Mg^{+2}$ (or $Fe^{+2}$) with $Na^+$ in the permutit process, and with $H^+$ in the ion-exchange process. The permutit process removes only the cations ($Ca^{++}$, $Mg^{++}$ or $Fe^{++}$) responsible for the hardness of the water; this process does not remove any anion, nor does it remove sodium or potassium ions that may be present in the hard water. (Rather, it adds more sodium ions to the water through the exchange process.) As a result, the water softened by this process is contaminated with sodium and potassium salts which, of course, do not impart any hardness to the water. This process cannot, therefore, de-ionise water completely. On the other hand, in the ion-exchange process, all the extraneous cations and anions present in hard water are completely removed by the ion-exchange reactions in the cation-exchanger and the anion-exchanger respectively, leaving practically undissociated water only. So, this process effects complete de-ionisation of hard water treated by it.

**Estimation of hardness of water.**—Both temporary and permanent hardness generally occur simultaneously in a sample of natural water, and the combined effect is referred to as the *total hardness* of water. The degree of hardness, or its soap-precipitating power, depends mainly on the amounts of calcium and magnesium salts present in it. The analytical methods for estimating hardness report it in terms of $CaCO_3$ (ppm.), each degree of hardness corresponding with 1 part of $CaCO_3$ per one million parts of water. Higher the degree of hardness of a sample of water, more it is unsuitable for use for washing purposes and in boilers.

Hardness of water may be estimated by adding standard soap solution from a burrette (a small portion at a time), shaking after each addition, until a lather lasting for 2-3 minutes is formed (**Clark's method**). This gives the total hardness of water. The permanent hardness of the sample of water is measured by similar titration of the same volume of the boiled water. The difference between the two values gives the temporary hardness of the sample. Hardness of water is generally estimated now-a-days by complexometric titrations with ethylenediamine teraacetic acid (E.D.T.A. or Versene). A known volume of the water (sample) is acidified with dil. HCl and boiled for some time to expel $CO_2$. It is then cooled and neutralised with dil. NaOH solution, and a few ml. of the buffer solution ($NH_4OH+NH_4Cl$, $pH=10$) are added. The solution is then titrated with 0.01 (M) E.D.T.A. solution with Eriochrome Black-T indicator, till the colour changes from wine-red to blue.

1 ml. of 0.01 (M) E.D.T.A. soln. = 1 mg. of $CaCO_3$. The results give the total hardness of the water. The permanent hardness of the sample may be estimated by similar titration of a known volume of the boiled (30 minutes) and filtered sample. The temporary hardness is obtained from the difference of the above two values.

**Pure water, conductivity water.**—Water for chemical and other scientific purposes should be very pure. The suspended and dissolved impurities in ordinary water are removed for these purposes by distillation from large copper retorts or from copper vessels provided with copper condensers. This water is known as *distilled water*. At present, such water is also prepared by using *de-mineraliser* or *de-ioniser*. Some gases like oxygen, carbon dioxide or ammonia may remain dissolved in distilled water. Ammonia is removed by passing chlorine gas into distilled water for some time and then boiling off chlorine. This water is then treated with a strongly alkaline solution of potassium permanganate and distilled, using condensers and flasks of pyrex glass. The middle fraction of the distillate is collected, which is very *pure* water and is also called *conductivity water*.

**Drinking water.**—Chemically pure water or distilled water (which is, in fact, very soft water) is tasteless and is not very conducive to health. Natural water, which is generally hard, is commonly used for drinking purpose. The dissolved salts present in such water impart refreshing taste and also health-giving quality to it. But, natural water is liable to be contaminated with substances which are harmful to living systems. It is, therefore, specially purified for making it suitable for drinking. The harmful substances which may be present in natural water are : (i) disease-causing bacteria and (ii) ammonia or other nitrogenous matter (from sewage), together with suspended impurities and poisonous substances.

**Purification of natural water for drinking purposes :**

The water supplied by the municipalities for drinking purposes are collected from rivers or lakes. These are first stored in large open tanks when much of the muddy substances is deposited at the bottom of the tanks. The water is then transferred to other such tanks and treated with alum (or aluminium sulphate) when all the fine suspended (colloidal) impurities are coagulated and settle at the bottom of the tanks, carrying with then some of the bacteria. The supernatant water is then filtered through filter-beds made of gravel and sand. The filtered water is then treated for destroying the bacteria by chlorination or chloramine process (or by ozonisation by treatment with ozonised oxygen or air). Any poisonous matter, if present in the water, is removed by suitable chemical methods.

**Drinking water from sea-water or brackish water :**

Extensive researches are being carried out to make sea-water (or brackish water) suitable for drinking purposes and for industrial uses. The following processes are being tried for the purpose :

(i) **Large-scale distillation process.**

(ii) **Use of special membranes** which permit the passage of pure water to pass through them but obstruct the passage of the dissolved salts.

(iii) **Freezing process** in which saline water is partially frozen, when ice made of pure water is formed, leaving behind the salts in the unfrozen water.

(iv) **Dehumidification process** in which dry air is passed over saline water. The pure water vapour, carried along with the air, is then condensed to liquid by bringing in contact with some cold surface.

**Tests.**—(i) Water turns white anhydrous copper sulphate blue. (ii) Water reacts with metallic potassium to evolve hydrogen which catches fire by the heat of the reaction. (iii) Water reacts with calcium carbide in the cold to give acetylene.

## COMPOSITION OF WATER.

(1) **Volumetric composition** : *Hofmann's method.*—Hofmann determined the volumetric composition of steam by sparking a mixture of hydrogen and oxygen in the volume-ratio 2 : 1 at a temperature higher than its condensation point (100°C). The apparatus used for this purpose is shown in Fig. 9.7.

A mixture of 2 vols. of hydrogen and 1 vol. of oxygen is introduced into the closed limb of the U-tube by displacement of mercury. This limb is surrounded by a jacket of a wider glass tube, through which amyl alcohol vapour (b.p. 132°C) is passed. After allowing some time for the gases in the closed limb to attain a steady temperature, their volume is noted by adjusting the levels of murcury in the two limbs. The open limb of the apparatus is then firmly closed by the thumb and electric sparks are passed into the gas-mixture through the two platinum wires sealed at the top of the closed limb. An immediate contraction in volume of the gases takes place, which is noted by adjusting the mercury levels. This contraction is found to be one-third of the original volume of the mixture of the gases. The passage of amyl alcohol vapour is then stopped and the temperature of the closed limb is allowed to come down below 100°C. Mercury level is seen to rise up slowly, and ultimately the closed limb is completely filled up by mercury. This is due to the fact that the two-thirds of the volume were occupied by steam which, when condensed to water, occupied practically no volume.

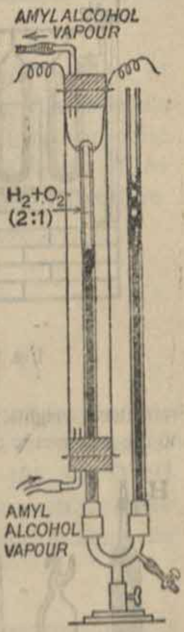


Fig. 9.7

It follows from the above observations that, 2 vols. of hydrogen combine with 1 vol. of oxygen to give 2 vols. of steam. So, the volumetric composition of steam (water) is, $H_2 : O_2 = 2 : 1$.

**Formula of water :**

The results show that, under the same condition of temperature and pressure,

2 vols. of hydrogen + 1 vol. of oxygen give 2 vols. of water (steam).

Applying Avogadro's hypothesis,

2 molecules of hydrogen + 1 molecule of oxygen give 2 molecules of water
or 1 ,, ,, ,, $+\frac{1}{2}$ ,, ,, ,, ,, 1 ,, ,, ,,
or 2 atoms ,, ,, +1 atom ,, ,, ,, 1 ,, ,, ,,
(∵ Hydrogen and oxygen molecules are diatomic.)

∴ Empirical formula of water $= (H_2O)x$. But, the vapour density of steam shows that its molecular weight is 18. Hence, the value of $x$ in $(H_2O)x$ is equal to 1. So, the *molecular formula* of steam is $H_2O$.

(2) **Gravimetric composition :** (i) *Dumas method.*—Dumas (1842) determined the gravimetric composition of water by passing hydrogen over weighed and heated copper oxide and weighing the water formed and the loss in weight of the copper oxide after the experiment. The assembly of apparatus used by Dumas is shown in Fig. 9.8.

Hydrogen, prepared by the action of dilute $H_2SO_4$ on zinc, was purified and dried by passing through a series of U-tubes containing lead nitrate solution, silver sulphate solution, caustic potash solution, conc. $H_2SO_4$ and phosphorus pentoxide etc. Pure and dry hydrogen was then passed over weighed copper oxide, kept in a previously weighed large vacuous bulb with long beak and heated with a large spirit lamp. The water formed was condensed in a glass bulb and the water vapour that escaped was absorbed in U-tubes similar to those used for drying hydrogen. The weight of water condensed in the bulb, together with the increase in the weights of the U-tubes after the bulb, gave the total weight of water formed. The loss in weight of the CuO-bulb gave the weight of oxygen consumed to form the water.

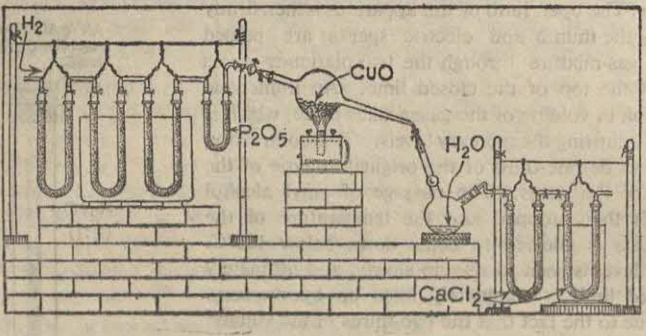


Fig. 9.8—Determination of gravimetric composition of water : Dumas method.

From these weights, the weight of hydrogen in the water produced was calculated and the gravimetric composition of water was thus determined.

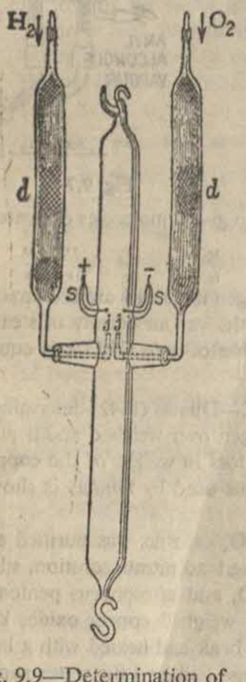
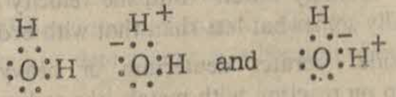


Fig. 9.9—Determination of gravimetric composition of water : Morley's method.

From a large number of experiments, Dumas found that the weight-ratio of oxygen to hydrogen in $H_2O$ was 7.98 : 1.

(ii) *Morley's method.*—Morely (1895) determined the most accurate gravimetric composition of water by using very pure hydrogen and oxygen. He measured the weight of each gas, as well as the weight of water formed by them on electric sparking. Pure and dry hydrogen, kept absorbed in palladium in a bulb, was weighed before and after the gas was expelled by heating into the reaction apparatus. Pure oxygen required for the combination was obtained from a glass globe which was also weighed before and after the experiment. The gases were led through two drying tubes *dd* (containing $P_2O_5$) to the reaction tube provided with two jets *jj* and a pair of wires *ss* connected to a power-source for sparking (fig. 9.9). During sparking, the reaction tube was cooled to condense the water formed by the combination. The liquid water was collected in the lower part of the tube. The tube was evacuated before and after the experiment, and the weight of water formed was thereby found out. (The exhaustion of the tube after the experiment expelled only the unreacted $H_2$ and $O_2$, as the loss of water vapour due to the expansion was prevented by $P_2O_5$). The residual unreacted $H_2$ and $O_2$ in the tube were estimated so that the actual weights of $H_2$ and $O_2$ that combined to form the weighed amount of the water were obtained. From the results of a number of experiments, Morley found that the ratio of weights of oxygen to hydrogen in water was 7.9394 : 1.

**The structure of $H_2O$ molecule** : Water has a dipole moment of the order of $1.71-1.97 \times 10^{-18}$ e.s.u. It thus indicates that the molecule is not linear, but angular. The two hydrogen nuclei and the mid-point of the oxygen atom form an angle of about 105°. The dipole of the water molecule is essentially the result of its non-linear structure. Three possible resonating structures of $H_2O$ molecules are :



which contribute (according to Pauling) 44%, 28% and 28% respectively to the total structure. The individual $H_2O$ molecule is represented commonly by an angular structure with the $\angle HOH = \sim 105°$ and O—H bond distance of 0.96Å. But, except in the vapour phase, such structure is non-existent due to extensive hydrogen bonding among the molecules.

**HEAVY WATER ($D_2O$)** : Heavy water or deuterium oxide is the $H_2O$-analogue of heavy hydrogen or deuterium, the atomic ratios in both the compounds being the same. It is prepared by electrolytic method. The electrolyte is the residual water of the electroytic cells used for the manufacture of hydrogen. This residual water is distilled and the distillate is made alkaline (0.5N) with NaOH. The alkaline water is electrolysed with nickel electrodes in seven stages. In the first stage, the electrolyis is carried out till the volume is reduced to about one-sixth the original. The electrolysis is then stopped and the alkali neutralised with $CO_2$ and the water distilled. The distillate is added to a further group of cells where the composition is the same. After three successive electroysis in the above manner, the deuterium-content of the electrolyte increases to such an extent that the liberated gases contain appreciable amounts of heavy hydrogen or deuterium. Such gases are, therefore, sparked and the condensed water is returned to appropriate stages of electrolysis. Continuation of such process makes the $D_2O$-content about 99% at the seventh stage of the electrolysis. Heavy water is manufactured in India by Bhaba Atomic Research Centre.

**Properties.**—Heavy water is a colourless liquid. It differs from ordinary water in many physical properties as shown below :

| **Property** | **$H_2O$** | **$D_2O$** |
|---|---|---|
| Sp. gravity (20°C) | 0.9982 | 1·1059 |
| Freezing Point (°C) | 0 | 3.82 |
| Boiling Point (°C) | 100 | 101.42 |
| Temp. of max. density (°C) | 4 | 11.6 |
| Vapour Pressure (mm.) at 20°C | 17.535 | 15.2 |
| Viscosity (millipoise) at 20°C | 10.09 | 12.6 |

**Reactions of deuterium oxide** : Deuterium oxide gives all the characteristic reactions of ordinary water. But, the velocity of the reactions with $D_2O$ is generally somewhat less than that with ordinary water.

Deuterium oxide liberates deuterium or heavy hydrogen on electrolysis and also on reaction with metals like sodium, calcium *etc.*

$$2D_2O \xrightarrow{\text{electrolysed}} \underset{\text{(At cathode)}}{2D_2} + \underset{\text{(At anode)}}{O_2}$$

$$2D_2O+2Na=D_2+\underset{\text{(Sodium deuteroxide)}}{2NaOD}$$

The metal deuteroxides (corresponding to the metal hydroxides) are formed by the action of $D_2O$ on the corresponding metal oxides : $Na_2O+D_2O=2NaOD$. The oxy-deuterium acids, such as $D_2SO_4$, $D_3PO_4$ *etc.* (corresponding to $H_2SO_4$, $H_3PO_4$ respectively) are obtained by the action of $D_2O$ on the corresponding anhydrides : $SO_3+D_2O=D_2SO_4$. Deuteroammonia ($ND_3$) and deuterium sulphide ($D_2S$) are formed when $D_2O$ reacts with magnessium nitride and anhydrous aluminium sulphide respectively : $Mg_3N_2+6D_2O=3Mg(OD)_2+2ND_3$ ; $Al_2S_3+6D_2O=2Al(OD)_3+3D_2S$. Deuteromethane ($CD_4$) and deuteroacetylene ($C_2D_2$), corresponding to $CH_4$ and $C_2H_2$, are formed by the action of heavy water on aluminium carbide ($Al_4C_3$) and calcium carbide ($CaC_2$), just in the analogous manner of the formation of $CH_4$ and $C_2H_2$ respectively Deuterium chloride, DCl (analogous to HCl), is easily formed by the action of $D_2O$ on benzoyl chloride or $PCl_3$ : $C_6H_5COCl+D_2O=C_6H_5COOD+DCl$ ; $PCl_3+3D_2O=D_3PO_3+3DCl$. The preparation and isolation of the above-mentioned deuterium compounds lead to the preparation of further varieties of deutro-compounds. For example, deuterium peroxide ($D_2O_2$, corresponding to $H_2O_2$) is obtained by the interaction of $BaO_2$ and $D_2SO_4$ : $BaO_2+D_2SO_4=BaSO_4+D_2O_2$. Deuteronitric acid ($DNO_3$) is obtained by distilling $NaNO_3$ with $D_2SO_4$ : $NaNO_3+D_2SO_4=NaDSO_4+DNO_3$. Like $H_2O$, deuterium oxide also forms deuterohydrates with salts, *e.g.* $CuSO_4.5D_2O$ ; $Na_2SO_4.10D_2O$ ; $CaCl_2.6D_2O$ *etc.*

Deuterium oxide enters into many important **exchange-reactions.** If compounds containing ionically bound hydrogen are introduced into heavy water, the hydrogen undergoes rapid but partial exchange for deuterium at ordinary temperatures :

$$D_2O+HCl \rightleftharpoons DCl+HDO : H_2O_2+D_2O \rightleftharpoons D_2O_2+H_2O ;$$

$$NH_4^+ \xrightarrow{D_2O} NH_3D^+ \xrightarrow{D_2O} NH_2D_2^+ \xrightarrow{D_2O} NHD_3^+ \xrightarrow{D_2O} ND_4^+.$$

It has been observed that the H-atoms linked to carbon do not undergo exchange by D under ordinary conditions. Thus, in hydrocarbons like $CH_4$ or $C_2H_2$, no exchange-reaction takes place. In glucose, only the hydroxy hydrogens are exchanged. The hydrogen atoms in acetone are all exchanged by deuterium ; it is because of the enolisation of the compound.

The material HDO is intermediate between $H_2O$ and $D_2O$ and, consequently, has intermediate properties. It is formed by the exchange-reaction, $H_2O+D_2O \rightleftharpoons 2HDO$, at high temperatures, or by catalytic photochemical reaction, $H_2O+HD \rightleftharpoons HDO+H_2$.

The deuterium compounds resemble the corresponding hydrogen analogues quite closely, but they are characterised by their decreased volatilities, increased densities *etc.*

**Biological and physiological effects of Heavy water.**

Heavy water has a toxic effect at high concentrations. Tobacco seeds do not germinate in pure heavy water. Some sea animals (like fish) die when placed in heavy water. Mice and rats appear to feel more and more thirsty on drinking heavy water. But, in small concentrations, heavy water has a tonic effect.

*Uses of Heavy water* : Heavy water is used (i) for the preparation of heavy hydrogen (deuterium), (ii) for the study of mechanisms of chemical reactions and the metabolic processes in living organisms. (iii) It is also used as a *moderator* in nuclear reactors for slowing down the bombarding neutrons.

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## HYDROGEN PEROXIDE

*Formula* : $H_2O_2$ *Molecular weight*=34

*Discovered by Thenard* (1818)

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**OCCURRENCE** : Hydrogen peroxide occurs in traces in the atmosphere and in some *natural* waters.

**PREPARATION.**—Hydrogen peroxide is prepared by the action of an acid (*e.g.* dil. $H_2SO_4$) on a suitable metal peroxide, such as hydrated barium peroxide ($Ba_2O, 8H_2O$)* or sodium peroxide ($Na_2O_2$).

In fact, any acid which forms an insoluble barium salt (*e.g.* carbonic, phosphoric, hydrofluosilicic and hydrofluoric acids) may be used in place of sulphuric acid, when barium peroxide is taken for the preparation.

In the *laboratory*, hydrogen peroxide is prepared by the action of cold dilute sulphuric acid and hydrated barium peroxide :

$$BaO_2+H_2SO_4=BaSO_4+H_2O_2.$$

A thin paste of barium peroxide in water is slowly added with stirring to ice-cold dilute sulphuric acid until the final mixture is faintly acidic. (A little quantity of hydrochloric acid is added to make the reaction smooth.) The precipitated barium sulphate is filtered off. A 10—20% solution of hydrogen peroxide in water is thus obtained.

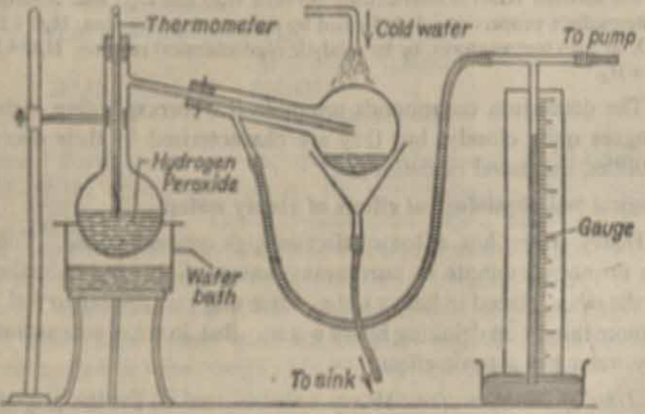

Fig. 9.10 Concentration of $H_2O_2$ solution under reduced pressure.

**Concentration** : The dilute solution of $H_2O_2$ is concentrated by evaporating in a glass or porcelain basin on water-bath till a 60% solution of hydrogen peroxide is obtained. Attempts for further concentration by this method decompose hydrogen peroxide. Further concentration is effected by successive distillations under reduced pressure (85°C/66mm.), when about 99% hydrogen peroxide is obtained.

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*Anhydrous barium peroxide does not easily react with dilute sulphuric acid due to the formation of an insoluble coating of barium sulphate on the particles of barium peroxide, which stops further reaction.

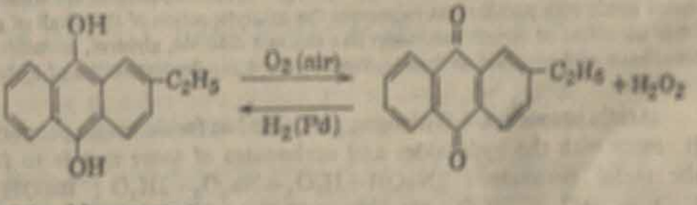
The product is stored by adding some preservative (glycerol or phosphoric acid) to minimize decomposition.

Pure hydrogen peroxide, which has only theoretical interest, can be obtained by drying 99% $H_2O_2$ in a vacuum desiccator over conc. $H_2SO_4$ and cooling the dried liquid with *dry ice* (solid $CO_2$), when solid $H_2O_2$ is formed.

**Manufacture of $H_2O_2$ : (i) Electrolytic method** : Hydrogen peroxide is largely manufactured by electrolysing ice-cold 40-50% $H_2SO_4$ under a high current-density with platinum electrodes, and then hydrolysing the resultant peroxy-disulphuric acid to hydrogen peroxide by steam distillation. A 30-40% aqueous solution of $H_2O_2$ is thus obtained, which may be concentrated by vacuum distillation. [The anodic oxidation of a mixture of ammonium sulphate in $H_2SO_4$, forming ammonium per-sulphate, and its subsequent hydrolysis gives better yield of $H_2O_2$.] $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$ ; $2SO_4^{2-} - 2e = S_2O_8^{2-}$ (at the anode). $2H^+ + 2e = H_2$ (at the cathode) ; $S_2O_8^{2-} + 4H_2O = 2SO_4^{2-} + 4H^+ + 2H_2O_2$.

**(ii) Auto-oxidation method :**

Hydrogen peroxide is also manufactured through the oxidation of 2-ethyl anthraquinol. A 10% solution of the anthraquinol in a mixture of benzene and cyclohexanol is oxidised by passing a stream of air through it, when 2-ethyl anthraquinone and $H_2O_2$ are formed. This is extracted with water and the solution of $H_2O_2$ (about 18%) is concentrated under reduced pressure. 2-ethyl anthraquinone, formed during the reaction, is reduced back to 2-ethyl anthraquinol by catalytic reduction in pressure of palladium (or Raney nickel), and it can be used again to undergo the cycle. The method is cheaper than the electrolytic method.



**(iii) Merck's process :**

The older manufacturing processes, which are also used to a limited extent, use (i) moist $BaO_2$ in conjunction with $H_2SO_4$ (or $H_3PO_4$), or (ii) $Na_2O_2$ and dil. $H_2SO_4$. In the latter process, which is known as the *Merck's process*, sodium peroxide is added in small portions to a 20% solution of $H_2SO_4$ cooled below 10°C. Conditions are so maintained that sodium sulphate produced in the reaction crystallises out as *Glauber's salt* ($Na_2SO_4.10H_2O$). This removes much of the water. The crystals are filtered off and the solution is concentrated under reduced pressure to obtain a 30% solution of $H_2O_2$ which is sold under the name, *Merck's perhydrol.*

**PROPERTIES OF HYDROGEN PEROXIDE : Physical properties.**—Anhydrous hydrogen peroxide is a colourless, syrupy liquid (*sp. gr.* 1.46), but it has a light blue colour in bulk. It boils at 151.4°C under normal atmospheric pressure, but it generally explodes when heated above 140°C. Pure hydrogen peroxide freezes to prismatic crystals at $-0.89$°C. It has an odour like that of nitric acid. It is miscible with water, alcohol and ether. Hydrogen peroxide is slightly acidic and turns blue litmus red.

**CHEMICAL PROPERTIES : Decomposition.**—At ordinary temperatures, hydrogen peroxide slowly breaks down into water and oxygen, with the liberation of considerable amount of heat. The decomposition is accelerated by heat and alkalis, and also in contact with rough surfaces, finely divided or colloidal metals like platinum and manganese or certain solids like manganese dioxide :

$$2H_2O_2 = 2H_2O+O_2+46{,}100 \textit{ calories.}$$

[The above decomposition of $H_2O_2$ is an *auto-oxidation-reduction process*, in which half of the oxygen atom of $H_2O_2$ (each with oxidation number of $-1$) are reduced to oxide ion (forming $H_2O$ where the oxidation number of the oxide ion is $-2$) and the other half of the oxygen atoms are oxidised to free oxygen ($\overset{o}{O}$, where its oxidation number is zero).]

The glass bottles used for storing hydrogen peroxide solutions are sometimes coated inside with paraffin wax to prevent the catalytic action of the alkali of glass. Small quantities of certain substances like calcium chloride, glycerol, acetanilide or phosphoric acid are used as *preservatives* to retard the decomposition of hydrogen peroxide.

**Acidic properties.**—Hydrogen peroxide has feeble acidic properties. It reacts with the hydroxides and carbonates of some metals to form the metal peroxides : $2NaOH+H_2O_2=Na_2O_2+2H_2O$ ; $Ba(OH)_2+H_2O_2 = BaO_2 + 2H_2O$ ; $Na_2CO_3 + H_2O_2 = Na_2O_2 + H_2O + CO_2$ ; $NH_3 + H_2O_2 = NH_4O_2H$.

Hydrogen peroxide acts both as an *oxidising* and a *reducing agent*, although the reducing action of hydrogen peroxide is only apparent, as it is not itself oxidised in such reactions. These apparent reductions should better be termed *de-oxidisation.* The oxidation number of oxygen in $H_2O_2$ is $-1$. As such, there is a tendency of its attaining the oxidation number of $-2$ units, as in the more stable $O^{2-}$ ion (reduction), or the oxidation number of zero, as in elemental oxygen (oxidation). Irrespective of the *p*H of the solution, $H_2O_2$ can act as a proton-acceptor (oxidising agent) or a proton-donor (reducing agent) as shown below :

In acid solution :

$H_2O_2+2H^++2e \rightarrow 2H_2O$ (oxidant), $E°=-1.77$ V.

$H_2O_2 \rightarrow 2H^++O_2+2e$ (reductant), $E°=-0.68$V.

In alkaline solution : $H_2O_2+2OH^-+2e \rightarrow 2H_2O+2O^{2-}$ (oxidant)

$H_2O_2+2OH^- \rightarrow 2H_2O+O_2+2e$ (reductant).

The oxidation by $H_2O_2$ in acidic solution is often slow, but it occurs with great rapidity in alkaline solution. The reducing property of $H_2O_2$ is manifested in reactions with materials which are themselves very strong oxidising agents, such as $KMnO_4$.

**Oxidising properties.**—Hydrogen peroxide is a powerful *oxidising agent.* It oxidises KI to iodine in acid solution : $H_2O_2+2HCl+2KI=2KCl+I_2+2H_2O$. In absence of acid, however, potassium hypoiodite is formed : $H_2O_2+KI=KIO+H_2O$. In acid solution, it oxidises ferrous salts to ferric salts : $2FeSO_4+H_2SO_4+H_2O_2=Fe_2(SO_4)_3+2H_2O$. Arsenious acid is oxidised to arsenic acid, sulphurous acid to sulphuric acid, hydrogen sulphide to sulphur and lead sulphide (*black*) to lead sulphate (*white*) by hydrogen peroxide :

$H_3AsO_3+H_2O_2=H_3AsO_4+H_2O$ ; $H_2SO_3+H_2O_2=H_2SO_4+H_2O$ ;
$H_2S+H_2O_2=2H_2O+S$ ; $PbS+4H_2O_2=PbSO_4+4H_2O$.

Hydrogen peroxide oxidises potassium ferrocyanide to potassium ferricyanide in acid solution :

$$2K_4[Fe(CN)_6]+H_2O_2+H_2SO_4=2K_3[Fe(CN)_6]+K_2SO_4+2H_2O.$$

Chromic acid ($K_2Cr_2O_7$+dil. $H_2SO_4$) is oxidised in the presence of ether to an unstable blue colour, the so-called *perchromic acid.* The colour is extractible with ether. This is a test for hydrogen peroxide.

**Reducing properties.**—In some of its reactions, hydrogen peroxide acts as a *reducing agent.* Thus, potassium ferricyanide is reduced to potassium ferrocyanide in alkaline medium :

$$2K_3[Fe(CN)_6]+2KOH+H_2O_2=2K_4[Fe(CN)_6]+2H_2O+O_2.$$

In acid solution, potassium permanganate is *quantitatively* reduced to manganous salt :

$$2KMnO_4+3H_2SO_4+5H_2O_2=K_2SO_4+2MnSO_4+8H_2O+5O_2.$$

Chlorine, ozone and silver oxide are reduced by $H_2O_2$ to hydrochloric acid, oxygen and metallic silver respectively :

$$Cl_2+H_2O_2=2HCl+O_2\ ;\ O_3+H_2O_2=2O_2+H_2O\ ;$$
$$Ag_2O+H_2O_2=2Ag+H_2O+O_2.$$

Bleaching powder, sodium hypochlorite and sodium hypobromite are also reduced in solution :

$$\underset{\text{Bleaching powder}}{Ca(OCl)Cl} + H_2O_2 = CaCl_2 + H_2O + O_2$$
$$NaOCl + H_2O_2 = NaCl + H_2O + O_2,$$
$$NaOBr + H_2O_2 = NaBr + H_2O + O_2.$$

**Formation of addition compounds.**—Hydrogen peroxide forms *addition compounds* with many salts like sodium sulphate, ammonium sulphate, potassium fluoride, sodium borate *etc.* They are known as *perhydrates.*

**Bleaching property.**—Hydrogen peroxide bleaches vegetable colours, straw, silk, feather and similar delicate articles by *oxidation*, without causing any damage to the materials.

**Strength of hydrogen peroxide solutions :** Commercial hydrogen peroxide is often referred to as of 10-vol., 20-vol., 100-vol. etc. strength. A 10-vol. hydrogen peroxide means that a given volume of this solution will give off 10 times its volume of oxygen at N.T.P., when decomposed. Other vol.-strengths are similarly defined. A simple calculation shows that a 10-vol. hydrogen peroxide solution contains 3.035 gms. of $H_2O_2$ per 100 ml. of the solution.

**Conversion of vol.-strength of $H_2O_2$ to percent strength and vice-versa.**

Inter-conversion of vol.-strength and percent strength of solutions of $H_2O_2$ can be easily done, as shown by the following examples :

(a) *Find out the strength of a 20-vol. $H_2O_2$ solution in gms. percent.*

Hydrogen peroxide decomposes according to the equation,

$$\underset{2\times 34\text{ gms.}}{2H_2O_2} = 2H_2O + \underset{22.4\text{ litres at N.T.P.}}{O_2}$$

68 gms. of $H_2O_2$, when decomposed, give 22.4 litres of oxygen at N.T.P. But, 100 ml. of a 20-vol. $H_2O_2$ solution will give (according to definition), 2000 ml. of $O_2$ at N.T.P. Now, 2000 ml. of $O_2$ will be evolved from $x$ gms. $H_2O_2$, where

$$22{,}400 : 2{,}000 = 68 : x$$

$$\text{or,}\quad x=\frac{68\times 2{,}000}{22{,}400}=6.07\text{ gms. of }H_2O_2.$$

So, 20-vol. $H_2O_2$ contains 6.07 gms. of $H_2O_2$ per 100 ml. of the solution.

(b) *Find out the vol. strength of a (N)$H_2O_2$ solution.*

A (N)$H_2O_2$ solution contains 17 gms. of $H_2O_2$ per litre.

[$\because$ the equivalent wt. of $H_2O_2$=17.]

So, 1 ml. of (N)$H_2O_2$ solution contains 0.017 gms. of $H_2O_2$.

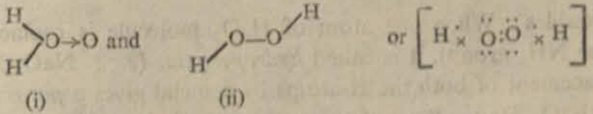
Now, 68 gms. of $H_2O_2$, when decomposed, give 22,400 ml. of $O_2$ at N.T.P.

$\therefore$ 0.017 gms. ,, ,, , ,, $\dfrac{22,400 \times 0.017}{68}$

$= 5.6$ ml. of $O_2$ at N.T.P.

So, we find that 1 ml. of (N)$H_2O_2$ solution (which contains 0.017 gms. of $H_2O_2$) gives 5.6 ml. of $O_2$ at N.T.P. Its vol. strength is, therefore, 5.6.

**Formula and structure of Hydrogen Peroxide.**—The estimation of the amount of oxygen formed by the decomposition of hydrogen peroxide indicates that the H : O ratio in its molecule is 1 : 1. The formula of hydrogen peroxide has been obtained as $H_2O_2$ from the measurement of its vapour density (17) and the freezing point depression of its solutions. The structure of $H_2O_2$ molecule has been a subject of much controversy. The following two structures are apparently possible for $H_2O_2$ :



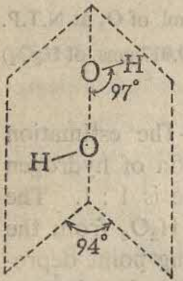
Structure (i) easily explains the weak ionisation of $H_2O_2$ in alkaline medium and the ready elimination of oxygen, as it is virtually a water molecule coordinated to an oxygen atom. But, this structure is not supported by X-ray spectrum of $H_2O_2$. Further, the following reactions also do not seem to support this structure : (a) $H_2O_2$ behaves as a dibasic acid, producing salts of two types, *viz.* NaO-OH and NaO-ONa, indicating thereby that there should be two -OH groups present in its molecule ; (b) $H_2O_2$ is formed by the action of dil. acids on metal peroxides which contain -O-O- bridge, and hence $H_2O_2$ should also have such peroxo-group ; (c) $H_2O_2$ gives diethyl peroxide on reacting with diethyl sulphate in alkaline medium. Diethyl peroxide produces ethyl alcohol on reduction with zinc and acetic acid. Such reactions are possible when $H_2O_2$ is constituted with two -OH groups joined together as in (ii), as with structure(i), diethyl ether should result as the product of above reduction.

$$\text{HO-OH} + (C_2H_5)_2SO_4 \longrightarrow C_2H_5\text{O-O}C_2H_5 \xrightarrow{2[H]} 2C_2H_5OH.$$

$$H_2O\rightarrow O + (C_2H_5)_2SO_4 \longrightarrow (C_2H_5)_2O\rightarrow O \xrightarrow{2[H]} (C_2H_5)_2O + H_2O.$$

So, structure (ii) is taken to represent $H_2O_2$ molecule. Thus, in the $H_2O_2$ molecule the O—O bond is a *p-p* σ-bond while the O—H bonds are *s-p* σ-bonds.

X-ray measurements indicate that O-O bond distance is 1.49 Å (same as O-O single bond distance) and each hydrogen is associated with each oxygen, but lying in two planes making an angle of 94° with each other. The H-O-O bond angle is 97°.* This configuration of $H_2O_2$ is shown in the marginal figure. Thus, the structure of $H_2O_2$ molecule is non-planar. The picture may be visualised as a book open apart at an angle of 94°, the O-O grouping lying on its spine, while the two H atoms lying on the outer surfaces of the two covers.



**Peroxides, Peroxyacids and their salts : Derivatives of $H_2O_2$.**—Hydrogen peroxide is the parent of a large number of compounds which are derived by the replacement of one or both hydrogen atoms of $H_2O_2$ by metals or acidic groups.

**Peroxides** : When one atom of $H_2O_2$ molecule is replaced by a metal (or $NH_4$ group), it is called *hydroperoxide* (*e.g.*, NaO.OH), and the replacement of both the H-atoms by a metal gives a *peroxide* (e.g., $Na_2O_2$, $BaO_2$ *etc.*). Both of these compounds have the *peroxo-group* in their molecules and they produce $H_2O_2$ on treatment with dilute mineral acids. These are distinguished from *dioxides* and *superoxides* by the facts that the dioxides (*e.g.*, $MnO_2$, $PbO_2$ *etc.*) do not form $H_2O_2$ with acids, but either form salts and water, or oxidise the acids (and hence do not contain the peroxo-bridge), and the superoxides (*e.g.*, $KO_2$) contain the grouping $O_2^-$. A true peroxide should correspond in formula to $M_2O_2$, where M is a monovalent positive ion.

**Peroxyacids and their salts.**—These compounds were earlier designated as *per-acids* and *per-salts.* The older nomenclature are not justified due to the fact that the prefix '*per*' is used to denote materials containing their central element in a higher state of oxidation than is normal for it (*e.g.* perclorate, $ClO_4^-$, permanganate, $MnO_4^-$ *etc.*), but not having any peroxy-linkages in the molecule. The replacement of one H-atom of $H_2O_2$ by an acid radical will give *peroxymono acid* (*e.g.*, $HO_3S$-O-OH, peroxymono-sulphuric acid), and the replacement of both the H-atoms of $H_2O_2$ by acid radicals will give *peroxydi acid* (*e.g.*, $HO_3S.O.O.O.SO_3H$, peroxydisulphuric acid). The replacement of hydrogen atoms of these peroxyacids with metals gives the corresponding *peroxy-salts*, *e.g.* $Na_2S_2O_8$, sodium persulphate. The following elements of the Periodic Table form peroxy acids :

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*According to some authors, the H—O—O bond angle is about 95° and the angle between the two planes containing the H—O—O groups is 97°.

| Group | III | IV | V | VI |
|---|---|---|---|---|
| | B | C, Ti, Zr, Ge, Sn. | N, P, V, Nb, Ta. | S, Se, Cr, Mo, W, U. |

The so-called permanganic acid ($HMnO_4$) and perchloric acid $(HClO)_4$ are not peroxy acids.

**Uses** : Hydrogen peroxide is used as an oxidising agent in chemical laboratories. It is also used for bleaching delicate materials like wool, silk, feather, ivory and hair. It acts as an *antichlor* to remove excess of chlorine from bleached fabric. Its valuable disinfecting properties are utilised for preparing mouth-washes and gargles with it. In admixture with petrol, hydrazine or alcohol, it is used as a rocket-fuel.

**Tests** : (i) $H_2O_2$ liberates iodine from acidified KI solution. It also liberates iodine from KI *in presence of $FeSO_4$*. The liberated iodine turns starch solution *blue*. (ii) $H_2O_2$ decolourises the pink colour of acidified $KMnO_4$ solution. (iii) $H_2O_2$ gives as orange-yelow colour with titanium sulphate solution. (iv) To a soln. of $K_2Cr_2O_7$, acidified with dil. $H_2SO_4$, is added a little $H_2O_2$. The mixture is immediately shaken with a small quantity of ether. A deep blue colour of the ether layer is formed.

CHAPTER X

# METALS AND METALLURGY

Metals are the main constituents of human civilization. Metals generally occur in nature in the combined state. Some three-fourths of all the chemical elements known are metals. They are lustrous solids at ordinary temperature (mercury is a liquid) and are electropositive in character. Metals are generally malleable and ductile, good conductors of heat and electricity and have high densities. [By itself, density is not a characteristic property of metals, for densities of metals vary from 0.6 for lithium to 22.5 for osmium]. Their oxides are generally basic in character and many of the metals evolve hydrogen on reacting with dilute mineral acids.

The characteristics of metals stated above are themselves the reflections of the type of bond that exists between the atoms of the metallic elements. The highly electropositive metals, occuring on the left-hand side of the Periodic Table, have relatively few electrons in their atoms available for bonding. They are thus unable to supply sufficient number of electrons to permit the formation of ionic or covalent bonds by loss (or gain) or sharing of electrons respectively among their atoms in a mass of the metal. Instead, the electrons of metals are exchanged back and forth among a large number of metal atoms, and indeed, move about through the solid metal with considerable ease. These *free* electrons constitute an *electron-gas* which serves to bound together the positive nuclei of the metal atoms, because each of them contributes one or more electrons to the gas and in turn receives electrons from other metal atoms. The resulting exchange of electrons binds together the entire mass, although no specific bonding, involving particular pairs of electrons, can be discerned. Such bonding has been termed **metallic bond.** (For details, see Chapter III). The degree of such bonding depends on the crystal structure of the metal, and this in turn depends principally upon the size of the atom of the metal. The **metallic state** is, therefore, recognised as a solid crystalline state in which the atoms are held together in their lattice-positions by the exchange energy of the electrons contributed by the atoms to form a pervading electron gas.

Mainly three types of crystal structure are represented among the metals. The simplest type is the *face-centred cube*, in which the atoms are arranged at the corners of a cube and at the very centre of each face of the cube. This type of crystal is characteristic of copper, silver, gold (and their solid solutions), calcium, aluminium, lead and platinum. Another type of crystal is the *body-centred cube* in which the atoms are placed at the eight corners and one atom is found in the exact centre of the cube. This type of crystal is characteristic of the alkali metals and also of barium. The third type of crystal is of the hexagonal close-packed structure, an arrangement that is assumed when a large number of solid balls are placed into a closed vessel, and they automatically arrange themselves in closest packing so that a minimum volume is attained. Light alkaline earth metals like Be, Mg, Ca and also Zn, Cd and Hg possess this type of crystal structure.

Many of the metallic characteristics can be easily explained from the above idea of the metallic state. The electrons of the metals in the common pool or electron-gas are only loosely bound, and hence interact with radiation in the visible region of the spectrum. Light is unable to penetrate beyond the first few layers of the atoms in the crystal before it is reflected quite completely. The metallic lustre and high opacity to visible light are accounted for in this way by the inherent electron behaviour. Again, the electrons are relatively free to drift from one end of the crystal to the other under the influence of an electric field, and indeed are free to cross the boundary of one crystal to another without much resistance. This explains the high electrical conductivity of metals. The increase of electrical resistance of a metal with the increase of temperature is explained by the fact that the thermally agitated atoms interfere with the easy passage of electrons through the crystal. As the *bonding* electrons in a metal cannot be considered to belong to any particular pair of atoms or indeed even to an individual atom, there is complete lack of directed valence in a metal, and hence the crystal may easily be deformed. This explains the malleability and ductility of metals.

**OCCURRENCE OF METALS : MINERALS AND ORES.**—Most of the metals occur in nature in the combined state, due to the fact that the common metals are susceptible to the attacks by moisture, carbon dioxide and oxygen *etc.* of nature. Metals like gold, platinum and silver are resistant to such attacks and as such, they are often found in the free state in nature. A metal is said to occur **native** or **free**, when it is found in nature in the metallic state, but this is of comparatively rare occurrence. In the combined state, the metals occur as **minerals or ores.** The name '**mineral**' is a general term, which means a naturally occuring substance containing *essentially* one of the chemical elements of interest (metal or non-metal), but the term '**ore**' is generally used to denote a naturally occuring substance from which a metal can be extracted economically on a large scale.

**Classification of ores.**—According to their states of combinations, ores (or minerals) can be classified as follows :

(1) *Oxide ores.*—Metals like copper, zinc, iron, aluminium, tin, manganese etc. occur in nature as oxides. Examples : Cuprite ($Cu_2O$), Zincite ($ZnO$), Tinstone or Cassiterite ($SnO_2$), Pyrolusite ($MnO_2$), Haematite ($Fe_2O_3$).

(2) *Hydrated oxide ores.*—Aluminium, iron etc. occur in nature as their hydrated oxides. Examples : Bauxite ($Al_2O_3.2H_2O$), Limonite ($2Fe_2O_3.3H_2O$).

(3) *Sulphide ores.*—Silver, copper, zinc, mercury, lead, tin, iron, cadmium etc. occur in nature as their sulphides. Examples : Copper pyrites ($2CuFeS_2$), Galena ($PbS$), Zinc blende ($ZnS$) *etc.*

(4) *Carbonate ores.*—Sodium, copper, calcium, magnesium, zinc, lead, iron etc. occur in nature as their carbonates. Examples : Malachite [$CuCO_3.Cu(OH)_2$], Limestone ($CaCO_3$), Dolomite ($CaCO_3.MgCO_3$), Calamine ($ZnCO_3$) *etc.*

(5) *Sulphate ores.*—Calcium, magnesium, lead, barium, strontium etc. occur in nature as their sulphates. Examples : Gypsum ($CaSO_4.2H_2O$), Kieserite ($MgSO_4.H_2O$), Barytes or Heavy spar ($BaSO_4$), Celestine ($SrSO_4$) *etc.*

(6) *Halide ores.*—Sodium, calcium, aluminium occur as their fluorides ; sodium, potassium, silver, magnesium, lead occur as chlorides ; silver also occurs as bromide. Examples : Cryolite ($AlF_3.3NaF$), Fluorspar ($CaF_2$) *etc.*

(7) *Phosphate minerals.*—Calcium occurs as phosphate in nature.

(8) *Silicate minerals.*—Magnesium and aluminium occur as complex silicates in nature.

(9) *Nitrate minerals.*—Sodium and potassium occur in nature as their nitrates.

EXTRACTION OF METALS FROM THEIR ORES : METALLURGY.—The process (or processes) by which metals are extracted economically from their ores is called *metallurgy*. It includes mainly chemical and also a few physical operations.

The ores of metals are invariably associated with earthy or rocky materials as impurities, called **Gangue** or **Matrix.** The procedures adopted to separate these from the metallic portion are known as **Ore dressing.** Much of the ore can often be separated by breaking away the adherent earthy deposits by hammering and then by hand-picking the metallic portions. Impurities which are intimately mixed up with the ores can only be removed by processes included under the **concentration** of ores.

### Concentration of ores :

Concentration of ores may be effected in a variety of ways. In each case, big lumps of ores are crushed into smaller pieces so that they may be completely exposed to the action in the subsequent operations. They are sometimes pulverised into a very fine state by means of stone-breakers, crushing rolls or grinding (or pulverising) mills. The important methods of ore-concentration are :

(a) *Washing.*—When suspended in or agitated with water, the denser metallic matter is less readily carried forward by a running stream of water than the lighter non-metallic portion. This causes a good separation of non-metallic impurities from the crushed ores.

(b) *Floatation processes.*—These processes are very useful for separating impurities which are intimately mixed with the ores. Finely divided materials in a state of admixture is introduced into water to which small quantities of a suitable oil or other materials able to make froth have been added. The water is then agitated violently with air, when a froth is formed which contains the particles of any solid materials affected by the oil or the other additions made. Pine or other oils, cresylic acid and xanthates are usually used as additives with water. These methods of treatment separates metallic materials, even when present in small quantities, from stony or siliceous materials. Copper pyrities, galena, zinc blende *etc.* are concentrated by these processes, when they are included in the froth formed.

(c) *Magnetic concentration.*—Iron and other ores, which are affected by magnetic influence, are separated in some cases by magnetic separators (Fig. 10.1). Some sulphide ores are not magnetic by themselves but become so on calcining them to oxides and thus become separable by this method. The crushed ore is brought into the magnetic field on a moving feed-belt. The magnetic portion is attracted by magnets, but is prevented from coming in contact with the magnets by the protective non-magnetic screen and drops on a receptacle just beyond the magnetic field. The non-magnetic portion remains unaffected and falls from the feed-belt into a separate receptacle. This method is employed in the metallurgy of tin.

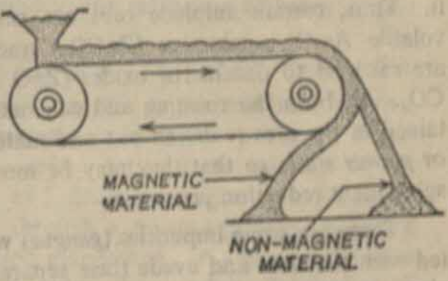


Fig. 10.1

(d) *Electrostatic concentration.*—The attractions and repulsions to and from an electrically charged surface depend on the ease with which induction and discharge of the material particles can take place. Obviously, the better conductors will be most readily affected, and by suitably regulating the movements of inclined charged surfaces, the metallic material may be separated from the non-metallic portions. This process has been gaining importance to effect concentration of ores.

(e) *Chemical method.*—The purification of *bauxite*, which contains iron, titanium, silica *etc.* as impurities, is effected by this method. The pulverised ore is digested with caustic soda solution at 150°C under pressure. Aluminium goes into solution as sodium aluminate. The impurities remain insoluble. Sodium aluminate solution is diluted, filtered and the filtrate digested with a little precipitated $Al(OH)_3$ with constant agitation, when pure $Al(OH)_3$ precipitates out. This is ignited to pure $Al_2O_3$ for the extraction of the metal.

**Calcination and Roasting.**—These two terms are often used loosely to mean the same operation. But, they are not exactly the same process.

**Roasting** is a process of heating an ore in presence of controlled amount of air below its fusion temperature to oxidise it ; *e.g.* zinc blende (ZnS) is *roasted* in air to convert it into zinc oxide (ZnO) or zinc sulphate ($ZnSO_4$).

**Calcination** is a process of heating an ore very strongly, at temperatures not sufficient to melt it, to drive off some volatile matter from it. Thus, certain sulphide ores are calcined to remove arsenic as volatile $As_2O_3$ ; calamine ($ZnCO_3$) and spathic iron ore ($FeCO_3$) are calcined to obtain the oxides (ZnO and $Fe_2O_3$) and to drive off $CO_2$. In both the roasting and calcination processes, moisture contained in the ores is driven out and materials are left in a more *open* or *porous* state, so that they may be more readily acted upon during subsequent reduction processes.

There are some impurities (*gangue*) which are tenaciously associated with the ores and evade their separation from the metals by the above processes. They are often refractory in nature and remain unaffected during various processes. These are separated by fusion in presence of some added material (flux). Although these impurities can stand high temperatures when heated alone, they react chemically with the *flux* at elevated temperatures to form easily fusible *slags*, which are generally removed by tapping out from the base of the furnace in which the operation is carried out.

**Flux** is a substance which is added to the ores to remove the impurities (as a fusible slag) after reacting with them at elevated temperatures. If the impurities are acidic in nature (*e.g.* silica or sand), basic fluxes like CaO or MgO are to be used, and if the impurities are basic in nature, acidic fluxes like silica are to be used. Neutral fluxes (like *fluorspar*, $CaF_2$) are sometimes used to maintain the fluidity of the molten ores, and to remove impurities like barytes and phosphate.

**Slag** is the fusible compound formed by the chemical reaction between the flux and the impurities in the ores.

Thus, **Flux+Gangue = Slag (or Cinder).**

**Reduction in metallurgy.**—The separation of a metal from its chemical combination is known as *reduction.*

Reduction is generally effected in various ways, *viz.*

(a) Chemical reduction, (b) Electrolytic reduction and (c) Metal displacement method.

(a) *Chemical reduction* : If the ore of a metal is available as the oxide, or if it can be transformed into an oxide by suitable methods of calcination or roasting, the isolation of the metal can be effected by heating the oxide with carbon or carbonaceous materials, such as charcoal, coal or coke. These substances react with the oxide of the metal, forming $CO_2$ or CO (according to the temperature of the operation). Carbon monoxide, in its turn, also reduces further quantities of the oxide to the metal. Such a process is called **carbon reduction process.** This is adopted in the extraction of many metals such as zinc, lead, tin, iron *etc.*

$Fe_2O_3+3C=2Fe+3CO$ ; $FeO+CO=Fe+CO_2$ ; $PbO+C=Pb+CO$.

Oxides of some metals like chromium, manganese, molybdenum *etc.* are generally reduced by **Thermit** process, where powdered aluminium is used as the reducing agent. An intimate mixture of the powdered oxide of the metal and finely granulated aluminium is ignited by a magnesium ribbon through a priming powder consisting of barium peroxide and pulverised magnesium. A rapid combustion ensues, producing $Al_2O_3$ and liberating the metal in the free state. A temperature as high as 2000°C is often attained, causing the liberated metal to melt. The molten metal is separated by suitable methods.

$$Cr_2O_3+2Al = Al_2O_3+2Cr.$$

In reducing the oxides of titanium, uranium *etc.*, metallic sodium is used as the reducing agent.

Sulphides of mercury (*cinnabar*) and silver are often reduced by **air-reduction process.** These sulphide ores are strongly heated in a current of air, when sulphur is oxidised to $SO_2$ and escapes as a gas, and the metal is set free (in the case of mercury, the metal is also vaporised, but it is subsequently condensed).

$$HgS+O_2 = SO_2+Hg.$$

The reduction of sulphide ores of copper and lead is effected by the **self-reduction process.** The sulphides are at first partly oxidised to form some amount of oxides and sulphates. The mutual reactions of the oxides, sulphides and sulphates at higher temperatures produce the metals. As no external reducing agents are used, this process is known as the **self-reduction process.**

$$2PbS+3O_2=2PbO+2SO_2\ ;\ PbS+2O_2=PbSO_4\ ;$$
$$PbS+2PbO=3Pb+SO_2\ ;\ PbS+PbSO_4=2Pb+2SO_2.$$

(b) **Electrolytic reduction** : The oxides of aluminium, calcium, magnesium *etc.* cannot be reduced to the metallic state by reduction with carbon or carbonaceous materials, due to the formation of carbides. In these cases, electrolytic reduction method is resorted to. Thus, for the extraction of aluminium from purified bauxite, the oxide is dissolved in fused *cryolite* ($3\ NaF.\ AlF_3$) and a little $CaF_2$, and the fused mass is electrolysed, when aluminium is liberated at the cathode. In the metallurgy of calcium or magnesium, the electrolysis is carried out with fused chlorides ($CaCl_2$ or $MgCl_2$), when the metals are liberated as usual in the cathode. Similarly, sodium is extracted by the electrolysis of fused sodium chloride or fused sodium hydroxide.

$$2Al_2O_3 \rightleftharpoons 4Al^{+3}+6O^{2-}\ ;\ 4Al^{+3}+12e \rightarrow 4Al\ ;\ 6O^{2-}-12e \rightarrow 3O_2.$$
$$CaCl_2 \rightleftharpoons Ca^{+2}+2Cl^-\ ;\ Ca^{+2}+2e \rightarrow Ca\ ;\ 2Cl^- -2e \rightarrow Cl_2.$$
$$2NaCl \rightleftharpoons 2Na^+ +2Cl^-\ ;\ 2Na^+ +2e \rightarrow 2Na\ ;\ 2Cl^- -2e \rightarrow Cl_2.$$
$$NaOH \rightleftharpoons Na^+ +OH^-\ ;\ Na^+ +e \rightarrow Na\ ;\ OH^- -e \rightarrow [OH]\ ;$$
$$4[OH] \rightarrow 2H_2O+O_2.$$

The above method of extracting a metal from its combination by electrolysis is called **electrolytic reduction.**

Electrolytic reduction is also employed in *the wet process* of extracting zinc from its sulphide ore. The sulphide ore is converted into the metal sulphate by aerial oxidation by heating, and the sulphate is leached with water or dilute $H_2SO_4$ solution. The resultant acidic clear solution is then electrolysed with proper electrodes, when the metal is deposited at the cathode.

(c) **Metal displacement method** :

This method is sometimes employed for the extraction of copper from its low-grade sulphide ore. The ore is aerially oxidised to copper sulphate, leached with dilute $H_2SO_4$ and the resultant clear solution is treated with scrap iron to precipitate copper.

$$CuSO_4+Fe=FeSO_4+Cu\downarrow.$$

Cadmium is obtained by this method by adding metallic zinc to the spent electrolyte collected in the cells for electrolytic refining of zinc. (The spent electrolyte is rich in cadmium.)

$$Cd^{++}+Zn=Zn^{++}+Cd\downarrow.$$

Silver and gold are extracted by such displacement method from their complex salt solutions.

$$2K[Ag(CN)_2]+Zn=K_2[Zn(CN)_4]+2Ag\downarrow.$$
$$2K[Au(CN)_2]+Zn=K_2[Zn(CN)_4]+2Au\downarrow.$$

In metallurgy, the processes of calcination or roasting and reduction are sometimes collectively known as **smelting.**

**Refining or Purification of crude metals.**—Metals extracted from their ores by some of the above processes are often contaminated with impurities, such as very small amounts of other metals and non-metals, unconverted oxides or sulphides, dissolved gases or even small amounts of slags. Refining of crude metals is carried out to remove these impurities, when the desired metal is obtained in a very high state of purity. Two methods are generally used for refining—either individually or in combination—depending upon the nature of the impurities and the degree of purity of the product required. These are : (a) *Thermal refining* and (b) *Electro-refining.*

(a) **Thermal refining.**—When the impurities present in the crude metal are easily oxidisable, they are removed by passing air through the molten mass of the crude metal (as in the case of copper and cupellation of silver) ; if, on the other hand, the metal is more volatile than the impurities present, it is separated by distillation, as in the cases of zinc and mercury.

Both these cases are examples of thermal refining, which is effected by heat.

**Zone refining** is a special case of thermal refining, and is used to prepare ultra-pure metals necessary for certain special purposes. The technique essentially consists of causing a narrow molten zone of a rod of the metal to move slowly from one end to the other. The effectiveness of the purification depends upon the difference in solubility of the impurities in the solid and the molten metal. As a result of the process, the impurities are concentrated in a short section at one end of the metal rod. This section of the rod is discarded and the remaining portion of the rod contains the metal in a very high state of purity.

In the **vacuum arc furnace refining,** the impure metal, in the form of an electrode, is gradually melted in the heat of the arc furnace under vacuum. During this process, the volatile impurities boil off. The pure molten metal is then chilled by pouring into water. Metals like titanium, zirconium and molybdenum are refined by this process.

**Vapour-phase refining** is employed in the purification of nickel. The finely divided impure metal is heated at 60°—80° in a current of carbon monoxide. The resultant volatile nickel carbonyl is decomposed by heating at 180° to form the pure metal.

$$Ni+4CO \xrightarrow{60°-80°C} Ni(CO)_4 \xrightarrow{180°C} Ni+4CO\uparrow .$$

**The Van Arkel process** is utilised to purify certain metals like Zr, Hf and Ti. For example, impure zirconium metal is heated in an evacuated glass vessel at 600°C with a small quantity of iodine. $ZrI_4$, thus formed, is vaporised at the prevailing temperature. The vapours of $ZrI_4$ is allowed to come in contact with a tungsten filament heated at 1800°—2000°C, when $ZrI_4$ decomposes into pure zirconium metal and iodine (vapour). The pure metal deposits on the tungsten filament.

$$Zr+2I_2 \overset{600°C}{=} ZrI_4(vapour)\ ;$$

$$ZrI_4 \overset{1800C°}{=} Zr+2I_2\uparrow .$$

(b) **Electro-refining of metals.**—Some metals are *refined* by an electrolytic process which is known as **electro-refining** of metals. In this process, an aqueous (acidic) solution of a salt of the metal to be refined is electrolysed with a block of the impure metal as the anode and a thin strip or a plate of the pure metal as the cathode. On passing current through the electrolytic cell, the ions of the metal under treatment dissolve out from the anode and deposit on the cathode. The impurities either remain in solution or are not dissolved, but gather as muddy deposits called *slime*, from which some valuable by-products are sometimes recovered.

In the electro-refining of copper, an aqueous solution of copper sulphate, acidified with dilute $H_2SO_4$, is electrolysed with blocks of impure copper as anodes and thin plates of pure copper as cathodes. From the *slime* of this process, valuable elements like gold, silver, antimony, bismuth, selenium, tellurium, *etc.* can be recovered. Copper deposited at the cathode is about 99.99% pure.

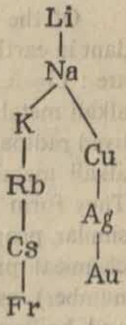
Zinc, extracted by carbon-reduction process may also be similarly refined by electrolysing an acidified solution of zinc sulphate or zinc chloride, with impure zinc blocks as anodes and pure zinc plates as cathodes. The metal deposited at the cathode is about 99.95% pure.

Crude aluminium is further refined by electrolytic processes (Hoope's process) to get about 99.99% pure metal.

CHAPTER XI

# ELEMENTS OF THE FIRST GROUP

Group I of the Periodic Table contains nine elements, all of which are metals, and they have been divided into two sub-groups, A and B. The first two metals, *viz.* lithium and sodium, are the *typical elements* of the group, but are very similar to the metals, potassium, rubidium, cesium and francium, and as such, these six metals comprise the sub-group A, which is the main sub-group of Group I. The other three metals, *viz.* copper, silver and gold, constitute the sub-group B. As the hydroxides of the principal members of the sub-group A have long been known as *alkalis*, the metals contained in this sub-group are grouped together under the common name, the **alkali metals**. The metals of the sub-group B have been used from early times in the preparation of coins, and as such they are called the **coinage metals** or the **currency metals.**



**Dissimilarities and similarities between Group IA and Group IB metals.**

**Dissimilarities :**

Very few resemblances are noticed between the members of the two sub-groups of the elements; rather, the contrasts are very prominent. The following differences are apparent : (i) the important and only valency exhibited by the alkali metals is 1, while the coinage metals show variable valencies, 1 and 2 for copper, 1, 2 and even 3 for silver and 1 and 3 for gold ; (ii) the alkali metals are very reactive, capable of displacing other metals from their combinations, and are readily oxidised by air, while the coinage metals are least active of the metals known, easily displaced from solutions of their salts by other metals and are very little oxidised in air ; (iii) the alkali metals never occur in nature in the free state due to their high reactivity, but the coinage metals often occur native in nature ; (iv) the alkali metals are strong base-formers and their halides are little hydrolysed in aqueous solutions, but the oxides and hydroxides of the coinage metals (except Ag) are feebly basic and their halides are hydrolysed (except silver halides) in aqueous solutions ; (v) the oxides, sulphides and cyanides of the alkali metals are soluble in water, while those of the coinage metals are not ; (vi) the alkali metals are never found in anions and they rarely form complex cations. But, the coinage metals are very prone to form complex ions, both cations and anions.

**Similarities :**

The similarities between sub-groups A and B are less striking. (i) The atoms of both these groups possess the valence-shell electronic configuration of $ns^1$, (ii) the crystal-forms of some salts of the elements of the two groups are isomorphous, showing some deep-seated resemblance between them. ($Na_2S$ and $Ag_2S$, $Na_2SO_4$ and $Ag_2SO_4$, NaCl, CuCl and AgCl are isomorphous.)

## THE ALKALI METALS.

Of the six alkali metals, sodium and potassium are quite abundant in earth's crust ($Na = 2.83\%$, $K = 2.59\%$) ; the occurrence of others are : $Li = 6.5 \times 10^{-3}\%$, $Rb = 3.1 \times 10^{-2}\%$, $Cs = 7 \times 10^{-4}\%$ ; the heaviest alkali metal, francium, occurs in nature in minute amounts as a short-lived radioactive substance. Due to their high chemical reactivity, the alkali metals are invariably found in nature in the combined state. They form the most homogeneous group in the Periodic Table, with similar properties. They exhibit a regular gradation in physical and chemical properties with the increase in atomic weight (or atomic number), as envisaged in the Periodic Law. Thus, the melting points and boiling points of the alkali metals continuously diminish from lithium to cesium, while the densities progressively rise from Li to Na, then show a break (K being lighter than Na) and then again rise upto Cs. The chemical activities, including basicity, of these elements increase with the increase of atomic weights of the elements.

**The electronic configuration of the atoms of the alkali metals :**

| Metal | At. No. | Electronic configuration | |
|---|---|---|---|
| Lithium | 3 | $1s^2 2s^1$ | or [He] $2s^1$ |
| Sodium | 11 | $1s^2 2s^2 2p^6 3s^1$ | or [Ne] $3s^1$ |
| Potassium | 19 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ | or [Ar] $4s^1$ |
| Rubidium | 37 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ | or [Kr] $5s^1$ |
| Cesium | 55 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ | or [Xe] $6s^1$ |
| Francium | 87 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6$ $5d^{10} 6s^2 6p^6 7s^1$ | or [Rn] $7s^1$ |

It is seen from the electronic configuration of the atoms of the alkali metals that, each of them contains a single *s*-electron in its outermost (valence) shell. Such a similarity in the electronic structure of the atoms results in remarkable alikeness of the physical and the chemical properties of these elements.

Some important physical properties of the alkali metals are shown in the following table :

TABLE 11.1

| Property | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| Atomic number | 3 | 11 | 19 | 37 | 55 |
| Atomic weight | 6.94 | 23.0 | 39.1 | 85.4 | 132.8 |
| Density at 20°C | 0.535 | 0.971 | 0.862 | 1.532 | 1.90 |
| Electronic configuration | 2.1 | 2.8.1 | 2.8.8.1 | 2.8.18.8.1 | 2.8.18.18.8.1 |
| Melting pt. (°C) | 179 | 97.9 | 63.5 | 39.0 | 28.45 |
| Boiling pt. (°C) | 1336 | 882.9 | 757.5 | 700 | 670 |
| Ionization potential (ev.) | 5.39 | 5.138 | 4.339 | 4.176 | 3.893 |
| Electronegativity | 1.0 | 0.9 | 0.8 | 0.8 | 0.7 |
| Atomic radii (Å) | 1.225 | 1.572 | 2.025 | 2.16 | 2.35 |
| Ionic radii (Å) | 0.60 | 0.95 | 1.33 | 1.48 | 1.69 |
| Reduction potential (V) ($M^+ + e \rightleftharpoons M$) | —3.04 | —2.71 | —2.92 | —2.99 | —3.02 |
| Flame colour* | Crimson | Golden yellow | Violet | Red | Blue |

Coming in a group just after the inert gases, the atoms of the alkali metals have one only valence-electron in the outermost shell of their atoms ; so, they have a ready tendency to part with this electron to attain the stable electronic configuration of the inert gases, and thus become a monovalent cation. As a result, the cations of the alkali metals form the positive part in their compounds.

The effect of the electronic configuration of the alkali metal atoms is reflected in the gradation of their physical and chemical properties, as enumerated below.

**Gradation of physical properties :**

(i) **Atomic volume and atomic radii** : There is a single-electron in the outermost (valence) shell of the atoms of the alkali metals. The penultimate shell, except in the atom of lithium, consists of a stable electronic octet ; in lithium, however, the penultimate shell is a stable duplet like the inert helium atom. The strong screening effect of the

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*On strong heating, some electrons, lying in the inner shells of certain metals (or ions) become exited and move to the higher energy shells. When these exited electrons come back to their original shells, the extra energy is released. This released energy forms distinct visible colour of the flame.

$s^2p^6$ electron-octet of the penultimate shell of the atom of an alkali metal largely protects the lone valence-electron from the attractive force of the nucleus. As a result, this electron can reside at a large possible distance from the nucleus and is attached quite loosely to the nucleus. Further, after the complete filling up of the outermost electronic shell in inert gas atom, the next alkali metal of Group IA is formed by the addition of an electron in a next higher energy shell of larger radius. As an obvious consequence, the atomic volumes and the atomic radii of the alkali metals are larger than those of the elements of other groups of the periodic table. As a result, the alkali metals occupy the highest positions in the different crests of the Lothar Meyer's atomic volume curve.

With the gradual increase of the atomic number of the alkali metals of Group IA, a new higher and larger energy shell is called into play for each higher element.

The increase in the number of filled inner shells also increases the screening effect on the nuclear attraction of the outermost electron. As a result of combination of these two factors, there is a gradual increase in the atomic volume and atomic radius from lithium to cesium.

(ii) **Ionisation potential** : Due to the large distance of and the less nuclear attraction on the outermost (valence) electron of an alkali metal atom (the reasons for which have been stated above), this electron is comparatively loosely attached in the atom. As a result, it can be easily removed to produce the monopositive ion ($M - e \rightarrow M^+$) by the application of small energy. So, the ionisation potential of the alkali metals is less than that of the other elements of the periodic table. As we move downward in Group IA from Li to Cs, the atomic radius increases, resulting in the increase of the distance of the $ns^1$ electron from the nucleus. As a result, the attraction of the nucleus on this electron gradually decreases. So, the ionisation potential of the alkali metals decreases from Li to Cs.

The **ionic radius** of an alkali metal ion is much less than its atomic radius, due to the fact that, the next lower electronic shell of the corresponding inert gas is exposed in the process of this ionisation. As a result, the ionic radius increases from Li to Cs.

(iii) **Density and Hardness** : It is generally observed that, in the case of the metals of Group IA (alkali metals), there is a gradual increase in the density and a gradual decrease in the hardness as the atomic number of the element increases.

(iv) **Melting and Boiling points** : The melting and the boiling points of the alkali metals gradually decrease as their atomic numbers increase.

(v) **Change in metallic character** : Strong metallic character of the Group IA elements (alkali metals) is due to the combined effect of the large atomic volume and very small ionisation potential of their atoms. As a result, the metallic character gradually increases from Li to Cs. This trend of metallic character of these elements is reflected in

(a) the **ionisation potential** of the atom which decreases gradually from Li to Cs,

(b) the **electrical conductivity** of these elements which gradually increases from Li to Cs, and

(c) the **electronegativity** (though small) of the elements which gradually decreases from Li to Cs.

**Gradation of chemical properties :**

(i) **Valency and its nature** : For the reasons already stated (*viz.* (i) the larger atomic volume, (ii) low ionisation potential and (iii) the large screening effect of the inner electron-filled shells), the tendency of an alkali metal (M) to form its ion ($M^+$) by the process $M \rightarrow M^+ + e$, is quite high. The electronic configuration ($s^2p^6$) of the ion $M^+$ is the same as that of the preceding inert gas atom. Thus, the ion $M^+$ is very stable electronically and it is generally not possible to remove 1 or more electron from $M^+$ to produce higher-valent ions like $M^{+2}$, $M^{+3}$ *etc.* So, the valency of the alkali metals is restricted to *+1 unit* only. As we move from $Li^+$ to $Cs^+$, the charge on the ion remains the same, but its ionic radius gradually increases. So, the ionic character also increases accordingly.

The very low value of the $\frac{\text{charge}}{\text{radius}}$ ratio of the alkali metal ions is very unfavourable for the formation of covalent compounds by the alkali metals. So, they almost always form ionic compounds in +1 oxidation state. [Some covalent compounds of the type R—M (such as $CH_3Na$, $CH_3Li$ *etc.*) are, however, formed.] Due to the above reason, the alkali metals rarely form complex compounds. Some coordination complexes of the alkali metals with oxygen-containing ligands like salicylaldehyde, salicylic acid *etc.* are, however, known. But, even in these cases, the M—O bond is more ionic than covalent.

(ii) **Change in basic property** : The factors that determine the metallic character of an element also determine its basic property. So, the basic character of the alkali metals increases gradually from Li to Cs. This trend is manifested in the following fact :

As we move from Li to Cs, the basic property of the oxides of the type $M_2O$ and of the hydroxides of the type MOH gradually increases. Thus, $Cs_2O$ is more basic than $Li_2O$, and CsOH is more basic than LiOH.

(iii) **Chemical reactivity** : The chemical reactivity of the alkali metals increases with the increase of their atomic numbers. Thus, all the alkali metals decompose water at ordinary temperature with the liberation of hydrogen gas : $2M+2H_2O=2MOH+H_2\uparrow$. The violence of this reaction increases from Li towards Cs. As a result, so much heat is evolved in the reaction of water with K, Rb or Cs that the liberated hydrogen gas catches fire.

Similar is the trend of the reactivity of the alkali metals with hydrogen, halogens and sulphur :

$$2M+H_2 = 2MH$$

$$2M+X_2 = 2MX\ (X=F, Cl, Br, I)$$

$$2M+S = M_2S.$$

[Among the alkali metals, *only* Li forms a nitride directly on heating in nitrogen gas : $3Li+N_2=Li_3N_2$.]

(iv) **Affinity of the alkali metals for oxygen** : All the alkali metals have strong affinity for oxygen which increases gradually from Li to Cs. All of them form the monoxide ($M_2O$) on heating in a limited supply of air or oxygen : $4M+O_2=2M_2O$. When burnt in air, lithium forms $Li_2O$, sodium forms mainly $Na_2O_2$ (with a small quantity of $Na_2O$). With excess of air or oxygen, Li and Na form their peroxides ($Li_2O_2$ and $Na_2O_2$), but K, Rb and Cs form their super-oxides ($KO_2$, $RbO_2$ and $CsO_2$).

(v) **Reducing power** : The reducing power of a reductant depends on its tendency to lose or supply electron. As the capacity of losing an electron by an atom of the alkali metal is very high, all of them are strong reducing agents. (This is due to their low ionisation potential.) As this capacity or tendency to give up an electron increases gradually from Li to Cs, the reducing property of the alkali metals also increases in this manner. The reducing property of the alkali metals is so great that they can force a hydrogen atom (which is also a strong reducing agent) to accept their $ns^1$ electron and thus form ionic or saline hydride. In these hydrides, hydrogen is present as $H^-$ ion.

$$2M+H_2 = 2MH.$$

The reducing power of the alkali metals, placed near the top of the electrochemical series of the metals, is very high and as such, they can replace other metals from the salts of the latter.

(vi) **Formation of solid bicarbonates, bisulphites and polyhalides** : For reasons stated before, the alkali metals form stable simple ions of low charge : radius ratio. Only such ions can stabilise the weak anions like bicarbonate ($HCO_3^-$), bisulphite ($HSO_3^-$), tri-iodide ($I_3^-$) *etc.*, so that the solid salts of these anions with the ions of the alkali metals are available.

The low value of the ionisation potential, coupled with the small cationic charge and large radius of the $M^+$ ion (i.e. low value of the charge: radius ratio) produces an overwhelming tendency on the part of the alkali metals to form and remain as stable monopositive ion ($M^+$) in almost all of its compounds. Hence, for all practical purposes, **the chemistry of the alkali metals may be regarded as the chemistry of their ions.**

**Similarities among the alkali metals :**

The alkali metals do not occur in the free state in nature due to their high chemical reactivity.

The alkali metal ions are all colourless and so are their salts, unless the anions are coloured. They nearly always exhibit electrovalency, except in the organo-metallic compounds such as $CH_3Na$, $C_2H_5Li$ *etc.* They are all soft metals that can be easily cut with a knife, are readily fusible and show high conductivity. They dissolve in liquid ammonia to give highly conducting, deep blue solutions. The alkali metals have strong affinity for oxygen and the freshly cut bright surfaces of them quickly tarnish on exposure to air, forming a film of oxides and carbonates. They burn in excess of air or oxygen to give $Li_2O$, $Na_2O_2$, $KO_2$, $RbO_2$ and $CsO_2$. The colour of the higher oxides deepens from Li to Cs, being white for $Li_2O_2$, yellow for $Na_2O_2$, orange-red for $KO_2$ and dark brown for $CsO_2$. They decompose water energetically at ordinary temperatures, forming the corresponding metal hydroxides and $H_2$. With K, Rb and Cs, the reaction with water is so vigorous (exothermic) that the evolved hydrogen inflames. Due to their high reactivity, they directly combine with sulphur and halogens, forming the sulphides and halides respectively. Li alone combines directly with $N_2$, when heated, to give $Li_3N$. They all form salt-like hydrides when heated in a current of $H_2$. The normal carbonates of the alkali metals (except Li) are stable at high temperatures, and they are the only metals to form bicarbonates which are stable solids. They displace all other metals from their salts.

**Peculiarities of Lithium.**—As the first member of the family, lithium is found to differ in certain important aspects from the other alkali metals. These differences arise mainly from the small size of the atom or the ion of lithium. It resembles to some extent the second member of the next group of elements, *viz.* magnesium, obeying the so-called *diagonal relationship*. [Similar polarising power of Li and Mg is responsible for this.] Lithium is more hard than the other alkali metals. (Magnesium is also a hard metal.) Thus, lithium burns in air with a dazzling flame like Mg. It combines with nitrogen on heating (cf. Mg and Ca) to form the nitride, $Li_3N$, which is decomposed by water into LiOH and $NH_3$ : $Li_3N+3H_2O=3LiOH+NH_3$. Lithium hydride is far more stable than the other alkali metal hydrides and can be melted (668°C) without decomposition. Lithium hydroxide is less soluble in water than the other alkali metal hydroxides, and unlike them, is decomposed at red heat to $Li_2O$ and $H_2O$. Lithium burns in air or oxygen to form only $Li_2O$, while the other alkali metals form peroxides or superoxides. Lithium carbonate crystallises without *water of crystallisation* and is sparingly soluble in water. It is decomposed by strong heating into $Li_2O$ and $CO_2$, and it thus differs from the alkali metals and resembles the alkaline earth metals. Lithium forms the unstable bicarbonate only in solution. Lithium chloride is deliquescent and crystallises with 1, 2 or 3 molecules of *water of crystallisation*. In this aspect, it resembles $CaCl_2$ (the chlorides of other alkali metals are anhydrous in the crystalline state). LiCl is hygroscopic and soluble in some organic solvents, while the chlorides of the other alkali metals are non-hygroscopic and they are practically insoluble in organic solvents. Lithium flouride and phosphate are sparingly soluble in water, while the fluorides and phosphates of the other alkali metals are soluble in water. In this respect, Li resembles Ca. Lithium hydrosulphide (LiSH) is not stable under ordinary conditions, whereas the hydrosulphides of the other alkali metals are. Lithium is the only alkali metal that forms an imide, $Li_2NH$. Lithium sulphate, in constrast with the other alkali metal sulphates, does not form alums, and is not also isomorphous with these sulphates.

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## LITHIUM

*Symbol* : Li ; *Atomic No.*=3 ; *Atomic wt.*=6.94 ;

*Electronic configuration* : $1s^2.2s^1$.

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OCCURRENCE : Lithium has two isotopes, *viz.* $Li^6$ (7.3%) and $Li^7$ (92.7%). The most important lithium mineral is **Lepidolite** or *Lithia mica*, $Li_2(F, OH)_2.Al_2(SiO_3)_3$ and **Spodumene**, $LiAl(SiO_3)_2$. Other ores are **Petalite**, $LiAl(Si_2O_5)$, **Triphylite**, $(LiNa)_3 PO_4.(Fe Mn)_3 (PO_4)_2$, **Amblygonite**, $LiAl(PO_4)F$. The metal also occurs in traces in muscular tissues and lungs, milk, human blood, sea-water and in tobacco, coffee and sugar-beet plants. Arfvedson first isolated (1817) $Li_2O$ from the minerals petalite and spodumene, but the metal was first obtained by Bunsen and Mathiessen (1855) through electrolysis of fused LiCl.

**EXTRACTION** : The minerals of Li invariably contain other alkali metals, which are separated by taking advantage of the relatively high solubility of LiCl in organic solvents like ethanol, acetone, pyridine *etc.* and the insolubility of $Li_2CO_3$ in water. [Other alkali metal chlorides are sparingly soluble in these organic solvents and their carbonates are soluble in water.] In view of the high positive standard potential [$Li \rightarrow Li^+(aq.) + e$ ; $E^\circ = +3.02$ volts), the metal cannot be made by the electrolysis of aqueous solutions of lithium salts, which invariably produces LiOH. The metallurgy of Li, therefore, consists of two distinct operations, *viz.* (*i*) the isolation of pure LiCl and (*ii*) the electrolysis of this salt in the fused state.

(i) *Isolation of pure LiCl* : (*a*) *From Silicate ores, Lepidolite* and *Petalite.*—Lepidolite contains 2–6% lithium, while petalite contains 2–3% lithium. Finely divided ores are fused with a mixture of barium carbonate, barium sulphate and potassium sulphate. The fused mass separates into two layers—the heavier lower layer containing $BaSO_4$, $SiO_2$ and $Al_2O_3$, and the lighter upper layer containing sulphates of lithium, sodium and potassium, together with some other lighter substances. The upper layer is separated, cooled and extracted with water. Barium chloride solution is added to the water-extract to precipitate the sulphates as $BaSO_4$, which is filtered off. The filtrate, containing the chlorides of Li, Na and K, is evaporated to dryness, and the cooled dried mass is extracted with a mixture of alcohol and ether, which dissolves only LiCl and not the other chlorides. The extract in the organic solvents is evaporated to get pure LiCl.

*From Spodumene.*—Spodumene contains 4–6% lithium. The ore is first calcined at 1000°C and the cooled mass is finely powdered. The powdered ore is then digested with conc. $H_2SO_4$ at 350°C for some time, when silicates are transformed into $SiO_2$. The mixture is evaporated to dryness, cooled and leached with water. The water-extract contains $Li_2SO_4$, along with other water-soluble metal-sulphates. Calculated amount of $Na_2CO_3$ solution is now added to the water-extract to precipitate iron, aluminium, magnesium *etc.* The precipitate is filtered and to the clear filtrate is added excess of $Na_2CO_3$ solution to precipitate $Li_2CO_3$. It is filtered and dissolved in HCl, and the resultant solution evaporated to dryness to get solid LiCl, which may be recrystallised from alcohol, if necessary.

(*b*) *From Phosphate ore, Triphylite.*—Triphylite contains 2–4% lithium. The finely powdered mineral is decomposed by aqua-regia and the solution is then evaporated for a number of times with conc. HCl to remove $HNO_3$. The dry mass is extracted with hot water and the aqueous solution is treated with excess of milk of lime, to precipitate the heavy metal impurities. The precipitate is filtered off and the clear solution is treated with excess $(NH_4)_2CO_3$ solution, when lithium is precipitated as $Li_2CO_3$. This is filtered, dried and ignited and the residue is dissolved in HCl and the solution evaporated. The residue is extracted with a mixture of dry alcohol and ether. The extract is evaporated, when solid LiCl is obtained.

(ii) *Electrolysis of fused lithium chloride* : A mixture of dry LiCl and KCl (in the proportion of 3 : 2 by weight) is fused and the molten mass is electrolysed (6-12 volts) at 450°C in a porcelain bath with graphite anodes and iron cathodes. [KCl is added to decrease the melting point of LiCl.] Lithium deposits on the iron cathode, and is quickly removed and kept under kerosine oil. The metal obtained is about 99.5% pure. Chlorine is obtained in this process as a valuable by-product.

**PROPERTIES** : **Physical properties** : Lithium is a soft, white metal, easily tarnishing in air due to the formation of oxide and nitride. It is the lightest of all metals (sp. gr. 0.53) and has the highest melting and boiling points (179°C and 1336°C) among the alkali metals. It has an extra-ordinary high specific heat (0.784 cal./gm. at 0°C) and is a good conductor of electricity. Its compounds impart carmine-red colour to the flame.

**Chemical properties** : Lithium is chemically less reactive than sodium and potassium. It is oxidised by dry air at about 100°C to form $Li_2O$ ; the reaction, however, takes place at ordinary temperatures with moist air. It reacts slowly with water at ordinary temperatures (25°C) to form LiOH and $H_2$. It is acted upon by dilute mineral acids to form the corresponding lithium salts and hydrogen. When heated in hydrogen at 700-800°C, LiH is formed. Lithium combines with nitrogen on heating to form lithium nitride,—a reaction uncommon to the rest of the alkali metals. Other non-metals like carbon, sulphur, phosphorus and halogens react with the metal directly on heating to form the corresponding binary compounds, *viz.* carbide, sulphide, phosphide and halides. It dissolves in liquid ammonia and various amines to form deep blue solutions. The solution of the metal in liq. ammonia is catalytically decomposed (by Fe) to the amide, $LiNH_2$, which on heating gives the imide, $Li_2NH$. Alcohols react with lithium to give the alkoxides, LiOR and $H_2$. The metal also reacts with alkyl and aryl halides in dry benzene or petroleum ether to form organo-lithium compounds which resemble the Grignard reagent.

**USES** : Lithium is used to de-oxidize, de-sulphurize, and in general, to de-gas copper and copper-alloys. It is also used as an alloying ingredient in special alloys to increase the tensile strength and anti-corrosion properties of the alloys. Lithium hydride and lithium aluminium hydride are used as powerful reducing agents in organic chemistry. Organo-lithium compounds are used in a variety of organic syntheses in a much better way than the Grignard reagent. The $Li^7$ isotope is used in control rods in fast atomic reactors. The lighter isotope ($Li^6$) is used for the production of tritium ($_1H^3$). Lithia water and some other lithium salts are used as medicine in the treatment of gout.

## COMPOUNDS OF LITHIUM.

**Lithium Hydride, LiH.**—It is obtained as a white opalescent vitreous mass, on passing a stream of dry hydrogen over lithium at about 700°C. It is a hard substance, melting at 680°C and is chemically very active. It is readily decomposed by water to form LiOH and $H_2$ : $LiH+H_2O=LiOH+H_2$. It is a salt-like (*saline*) hydride, containing hydrogen as the anion ($H^-$), and can be electrolysed in the fused state to liberate lithium at the cathode and hydrogen at the anode. It is a strong reducing agent and is used as the highest source of hydrogen and for the preparation of lithium aluminohydride, $LiAlH_4$.

**Lithium Aluminohydride, $LiAlH_4$,** is prepared by the interaction between LiH and $AlCl_3$ in dry ether : $4\ LiH+AlCl_3=LiAlH_4+3\ LiCl$. It is a white solid, stable in dry air, but is readily decomposed by water into hydrogen and the hydroxides of lithium and aluminium : $LiAlH_4+4H_2O=LiOH+Al(OH)_3+4H_2$. It is also decomposed into LiH, Al and $H_2$ on heating at about 150°C. Lithium alumino-hydride is moderately soluble in dry ether. It is widely used as a reducing agent and in the preparation of other metallic hydrides.

Some typical reactions of $LiAlH_4$ are shown below :

(*a*) $2LiAlH_4+5NH_3 = [LiAlH(NH_2)_2]_2\,NH+6H_2$ ;

(*b*) $LiAlH_4+2B_2H_6 = LiBH_4+Al(BH_4)_3$ ;

(*c*) $3\ LiAlH_4+AlCl_3 = 4\ AlH_3+3LiCl$ ;

(*d*) $LiAlH_4+SnCl_4 = SnH_4+LiCl+AlCl_3$.

**Lithium Monoxide, $Li_2O$,** is obtained as a white powder on heating the metal in oxygen (or air) at about 200°C, or by heating its hydroxide, carbonate or nitrate at about 800°C in a current of dry hydrogen. It slowly dissolves in water to give the hydroxide, LiOH. On heating above 400°C, lithium monoxide disproportionates into lithium peroxide and metallic lithium : $2Li_2O \xrightarrow{>400^\circ C} Li_2O_2 + 2Li$. It reacts with dry ammonia gas, when heated, to form lithium amide and LiOH : $Li_2O + NH_3 = LiNH_2 + LiOH$.

**Lithium peroxide, $Li_2O_2$.**—Unlike $Na_2O_2$, lithium peroxide is not formed by heating the metal in excess of air or oxygen. The crystalline white product, $Li_2O_2.H_2O_2.3H_2O$, is obtained by adding $H_2O_2$ and alcohol to an aqueous solution of lithium hydroxide and drying the precipitate over fused calcium chloride. Lithium peroxide is a white solid which decomposes to pure $Li_2O$ and $O_2$ when heated at 300°C in vacuum.

**Lithium Hydroxide, LiOH**, is prepared by dissolving the monoxide ($Li_2O$) or the metal in water. It can also be obtained by adding baryta solution to a solution of $Li_2SO_4$ in water, filtering off the precipitated $BaSO_4$, and concentrating the filtrate, when LiOH, $H_2O$ crystallises out as a white solid : $Li_2SO_4 + Ba(OH)_2 = 2LiOH + BaSO_4$. The hydrated crystals may be made anhydrous by heating at 140°C in a current of hydrogen, but at 780°C, the monoxide $Li_2O$ is formed. LiOH melts at 445°C and is soluble in water, although the solubility is less than those of NaOH and KOH.

Lithium oxide and hydroxide are used in the preparation of photographic developers, and the hydroxide is used in alkali storage batteries.

**Lithium Nitride, $Li_3N$,** is a salt-like (saline) nitride, resembling the alkaline earth nitrides, and are formed by the reaction of the metal with nitrogen even at ordinary temperatures : $6Li + N_2 = 2Li_3N$. It is a grey hygroscopic substance and is decomposed by water to form LiOH and ammonia : $Li_3N + 3H_2O = 3LiOH + NH_3$. A red transparent variety of the nitride is formed on heating the metal at 850°C in a current of dry nitrogen.

**Lithium Amide, $LiNH_2$,** is obtained as a white crystalline substance on passing dry $NH_3$ gas over the metal at 400°C, or by the action of liquid ammonia on the metal. When heated in vacuum at 640°C, it is decomposed into lithium imide ($Li_2NH$) and ammonia : $2LiNH_2 = Li_2NH + NH_3$. Lithium imide is decomposed by water into LiOH and $NH_3$ : $Li_2NH + 2H_2O = 2LiOH + NH_3$.

**Lithium sulphide, $Li_2S$,** is formed as a light yellow amorphous product by the direct union of the metal and sulphur at elevated temperatures. It can also be prepared by reducing lithium sulphate with carbon : $Li_2SO_4 + 4C = Li_2S + 4CO$.

**Lithium carbonate, $Li_2CO_3$.**—This is obtained as a white powder on boiling a solution of a lithium salt in water with potassium carbonate or sodium carbonate or ammonium carbonate. Unlike the carbonates of other alkali metals, it is sparingly soluble in water and contains no water of crystallisation. It melts at 690°C and decomposes to $Li_2O$ and $CO_2$ at red heat : $Li_2CO_3 = Li_2O + CO_2$ (*cf.* the thermal decomposition of $CaCO_3$ to CaO and $CO_2$). When $CO_2$ gas is passed through a suspension of lithium carbonate in water, it dissolves to form lithium bicarbonate which is stable *only* in aqueous solution. [This solution is used for the treatment of gout under the commercial name 'lithia water'.) The aqueous solution of lithium bicarbonate decomposes on heating to evolve $CO_2$, with the precipitation of lithium carbonate :

$$2LiHCO_3 \rightleftharpoons Li_2CO_3 \downarrow + H_2O + CO_2 \uparrow .$$

It is used to prepare glass which is transparent to ultra-violet light.

**Lithium Fluoride, LiF** : It is formed as a white precipitate on adding ammonium fluoride solution to an aqueous solution of a lithium salt.

$$LiNO_3 + NH_4F = LiF \downarrow + NH_4NO_3.$$

**Lithium Chloride, LiCl,** is obtained as a white deliquescent solid, by decomposing lithium carbonate with dil. HCl, or by the double decomposition of lithium sulphate and barium chloride solutions: $Li_2CO_3 + 2HCl = 2LiCl + CO_2 + H_2O$ ; $Li_2SO_4 + BaCl_2 = 2LiCl + BaSO_4 \downarrow$. The clear aqueous solution of LiCl, obtained in either of the above reactions, is evaporated in a stream of HCl gas to obtain the anhydrous salt. It melts at 600°C and is highly soluble in water as well as in many organic solvents like alcohol, acetone, pyridine *etc.* (difference from the chlorides of other alkali metals). It crystallises as the anhydrous salt from boiling water, but at lower temperatures, the isolated crystals are associated with 1—3 molecules of water of crystallisation. The aqueous solution of the salt absorbs ammonia to form different *ammoniates*, with composition $LiCl.NH_3$, $LiCl.2NH_3$, $LiCl.3NH_3$ *etc.* It forms double salts with the chlorides of Fe, Mn, Co, Ni, Cu, U *etc.* Lithium chloride is used for extracting the metal. It is also used in making fireworks, in air-conditioning and in soldering metals like Al and Mg.

**Lithium Nitrate, $LiNO_3$,** is prepared as a highly deliquescent, colourless crystals, by dissolving $Li_2CO_3$ or LiOH in $HNO_3$ and crystallising the solution. It is highly soluble in water and alcohol. From aqueous solution, it crystallises with 3 molecules of water of crystallisation. The salt is decomposed to $Li_2O$ on heating :

$$4LiNO_3 = 2Li_2O + 4NO_2 + O_2.$$

**Lithium Sulphate, $Li_2SO_4$.**—This is formed on dissolving the metal or its hydroxide or carbonate in dil. $H_2SO_4$. It crystallises as the anhydrous salt from hot solutions, but as the monohydrate, $Li_2SO_4.H_2O$, at lower temperatures. It is a white solid, melting at 843°C and is highly soluble in water. It forms double sulphates with other alkali metal sulphates and with $CuSO_4$ and $Al_2(SO_4)_3$.

Other sparingly soluble salts of lithium, like phosphate, are prepared by adding solutions of the corresponding sodium salts to a solution of $Li_2SO_4$ in water. The precipitated salt is filtered, washed with water and dried in air.

**Tests** : Lithium salts give a crimson red colour in the **flame test.** Its presence is also detected by precipitation as fluoride, phosphate, carbonate or oxalate. It is estimated by weighing as $Li_2SO_4$.

## SODIUM

*Symbol* : Na ; *Atomic No.=11* ; *Atomic wt.=22.99.*

*Electronic configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^1$

*The metal was first isolated in 1807 by Davy.*

OCCURRENCE : Being a very reactive metal, sodium does not occur native. In combination with other elements, it is widely available as **sodium chloride** (NaCl) in sea-water and as rock-salt deposits. It occurs as **sodium nitrate** ($NaNO_3$) in *Chile saltpetre* or *Caliche.* Sodium carbonate ($Na_2CO_3$) is available as *natural soda deposits.* **Sodium aluminium fluoride** or *cryolite* (3NaF, $AlF_3$) and **sodium tetraborate decahydrate** or *borax* ($Na_2B_4O_7.10H_2O$) are also found in large quantities in nature.

EXTRACTION : Sodium is generally extracted through electrolysis of fused sodium hydroxide (**Castner Process**) or fused sodium chloride (**Down's Process**). [Electrolysis of aqueous solutions of NaOH or NaCl, no doubt, liberates metallic sodium at the cathode, but the metal immediately undergoes secondary reaction within the cell to give products other than metallic sodium.]

**Castner Process** : The cell used in this process is an iron vessel (Fig. 11.1) in which caustic soda is kept in the molten condition by heating with burners. An iron rod (C) acts as the cathode, which is firmly held in position by solid NaOH at the bottom. A cylinder of nickel (A, A) is suspended from the flange of the iron vessel (with proper insulation), round the upper part of the cathode, and this serves as the anode of the electrolytic cell. A chamber (E), elongated downwards with cylindrical wire-gauge (F,F), surrounds the cathode. Within the cell, the molten sodium hydroxide dissociates into $Na^+$ and $OH^-$ ions, and on passing electricity through the melt, the $Na^+$ ions migrate to the cathode and are liberated there as metal. Being lighter than the molten electrolyte, the metal rises to the surface (the outward diffusion being arrested by the cylindrical wire gauge) and collects in the chamber (E). It is removed from time to time with the help of a perforated ladle and collected under an inert liquid like kerosene oil. The $OH^-$ ions are liberated at the anode and are decomposed there into $H_2O$ and $O_2$. Oxygen escapes through the outlets (G,G) and hydrogen through the chamber (E) where it serves as a non-oxidising protective atmosphere for the molten sodium.

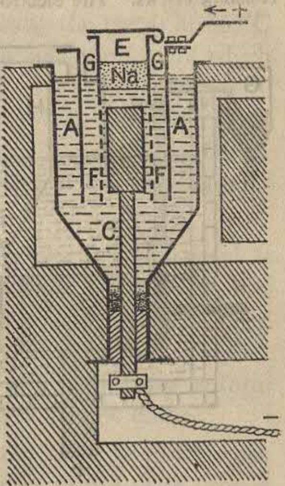

Fig. 11.1

$NaOH \rightleftharpoons Na^+ + OH^-$ ; $Na^+ + e \rightarrow Na$ (at *cathode*) ; $OH^- - e \rightarrow [OH]$ (at *anode*) ; $4[OH] \rightarrow 2H_2O + O_2$.

**Down's Process** : Sodium is extracted through the electrolysis of fused sodium chloride by this method. The extraction is, however, complicated due to the facts that, (i) NaCl melts at a very high temperature (800°C), which is very near the vaporising temperature of sodium (883°C), causing much loss of the metal through vaporisation, (ii) molten NaCl is a very corrosive liquid at 800°C and above, which results in extensive corrosion of materials commonly used for the preparation of the electrotylic cell and the electrodes, and (iii) the molten electrolyte dissolves some quantity of the metal liberated, at the temperature of the electrolysis. To minimize these complications, the melting point of NaCl is lowered to about 600°C by adding anhydrous $CaCl_2$ to the electrolyte. This lowers the corrosive action of the fused salt and also the solubility of sodium in the molten electrolyte.

The electrolytic cell (Fig. 11.2) consists of an iron-vessel, lined with acid-resisting bricks. The electrolyte (33.2% $NaCl+66.8\% \ CaCl_2$) is placed in the cell and melted by electrical heating. The anode (A) is a graphite rod which is surrounded by an annular iron-cathode (K), provided with wiregauge casing (D) which is connected by an iron-pipe (RF) to an iron-vessel (G) containing kerosene oil. A funnel-shaped porcelain hood (H), placed above the anode, serves as the outlet for the escape of $Cl_2$. On electrolysis, sodium is liberated at the cathode, and it rises up the siphon and overflows into the vessel (G).

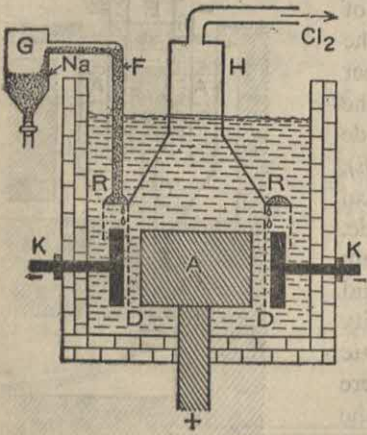

Fig. 11.2

$NaCl \rightleftharpoons Na^+ + Cl^-$ ; $Na^+ + e \rightarrow Na$ (at *cathode*) ; $Cl^- - e = [Cl]$ (at *anode*) ; $2[Cl] \rightarrow Cl_2$.

**Properties : Physical properties :** Sodium is a soft, white metal, melting at 98°C. Its density is 0.98 and is a good conductor of electricity. It dissolves in liquid ammonia to form a deep-blue solution. It can be cut with a knife and extruded as a wire when pressed through a small opening.

**Chemical properties :** It is unaffected by dry air, but is acted upon by moist air to form $Na_2O$ and $NaOH$, which are ultimately transformed into $Na_2CO_3$ by atmospheric carbon dioxide : $4Na+O_2=2Na_2O$ ; $Na_2O+H_2O=2NaOH$ ; $2NaOH+CO_2=Na_2CO_3+H_2O$. The metal is, therefore, stored under kerosene oil.

Sodium burns in air or oxygen with a golden yellow flame, forming $Na_2O$ and $Na_2O_2$ (with excess of air or oxygen, $Na_2O_2$ is formed as the main product). The metal reacts explosively with water to form sodium hydroxide and hydrogen : $2Na+2H_2O=2NaOH+H_2\uparrow$. Chlorine and sulphur react with the metal at elevated temperatures to form NaCl and $Na_2S$ respectively. When heated at 200-300°C in a current of dry ammonia, sodium forms sodamide : $2Na+2NH_3=2NaNH_2+H_2\uparrow$. (Sodamide is decomposed by water into ammonia and sodium hydroxide : $NaNH_2+H_2O=NH_3+NaOH$.) Being a strongly electropositive metal, sodium acts as a good reducing agent and liberates many metals from their combinations : $AlCl_3+3Na=3NaCl+Al$. It also dissolves certain metals to form alloys (solid or liquid).

**USES :** Sodium is used for the preparation of many of its useful compounds, *viz.*, $Na_2O_2$, NaCN, $NaNH_2$ *etc.* Metallic sodium is used as a reducing agent in metallurgy. It is also used for the detection of C, N, S and halides in organic compounds, as a condensing agent in many organic syntheses and also for drying alcohols. An alloy of sodium and potassium (liquid) is used in high-temperature thermometers, and the metal itself is used in sodium-vapour lamps.

## COMPOUNDS OF SODIUM.

**Sodium Hydride** (NaH) is prepared by heating the metal at 365°C in a current of pure and dry hydrogen. It is a colourless solid which decomposes on heating to high temperatures into sodium and hydrogen, and is acted on by water to produce NaOH and $H_2$ : $NaH+H_2O=NaOH+H_2\uparrow$. It forms sodium formate with $CO_2$ : $NaH+CO_2=H.COONa$. It is a strong reducing agent and is used in organic reduction or condensation reactions.

**Sodium Monoxide** ($Na_2O$) is obtained when sodium metal is heated in a limited quantity of air, the unreacted metal being distilled off *in vacuo*. A better method of the preparation is to fuse the metal with sodium hydroxide : $4Na+O_2=2Na_2O$ ; $2Na+2NaOH=2Na_2O+H_2\uparrow$. It is a white solid which reacts vigorously with water to form sodium hydroxide : $Na_2O+H_2O=2NaOH$. It is a basic oxide.

**Sodium Peroxide** ($Na_2O_2$) is obtained as the main product when metallic sodium is burnt in air (a small quantity of $Na_2O$ is formed during the combustion). It is prepared on a large scale by heating the metal at 300-400°C with excess of dry and $CO_2$-free air. Small slices of metallic sodium are kept on aluminium trays. With the help of a moving belt, these trays are slowly passed from one end to the other of a heated tube furnace. The temperature of the furnace is maintained at 300-400°C and a stream of dry and $CO_2$-free air is passed through one end of the tube of the furnace. During this process, metallic sodium is oxidised to sodium peroxide on the aluminium trays which come out through the other end of the tube furnace. The reaction being *exothermic*, external heating is discontinued after the reaction has started : $2Na+O_2=Na_2O_2$.

Sodium peroxide is a light yellow solid ; but, it becomes white when exposed to air due to the formation of a coating of NaOH and $Na_2CO_3$ over it. It dissolves in ice-cold water, forming sodium hydroxide and hydrogen peroxide in solution ; the reaction is, however, reversible : $Na_2O_2+2H_2O\rightleftharpoons 2NaOH+H_2O_2$. As the solution of $H_2O_2$ is unstable towards heat, especially in the presence of alkali, the $H_2O_2$ produced in the above reaction breaks up into $H_2O$ and $O_2$ on raising the temperature of the reaction. As a result, the reaction between water and $Na_2O_2$ at room temperature produces NaOH and $O_2$. With ice-cold mineral acids, $Na_2O_2$ yields hydrogen peroxide, and this reaction is used for the manufacture of $H_2O_2$ by **Merck's process** : $Na_2O_2+H_2SO_4=Na_2SO_4+H_2O_2$. Sodium peroxide is a strong oxidising agent, and oxidises heated charcoal to sodium carbonate : $3Na_2O_2+2C=2Na_2CO_3+2Na$. It also absorbs $CO_2$ to form sodium carbonate, and is, therefore, used as an *air-purifier* : $2Na_2O_2+2CO_2=2Na_2CO_3+O_2$. It oxidises chromic hydroxide to sodium chromate, manganous salts to sodium manganate and sulphides to sodium sulphate : $2Cr(OH)_3+3Na_2O_2=2Na_2CrO_4+2NaOH+2H_2O$. It forms sodium carbonate on reacting with carbon monoxide : $Na_2O_2+$

$CO = Na_2CO_3$ ; But, it reduces $KMnO_4$, a stronger oxidising agent, in acidic medium: $2KMnO_4 + 8H_2SO_4 + 5Na_2O_2 = K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 8H_2O + 5O_2$.

It reacts with anhydrous ethyl alcohol at 0°C to form sodium hydro-peroxide as a white powder :

$C_2H_5OH + Na_2O_2 = C_2H_5ONa + NaOOH$.

Sodium peroxide is used for the manufacture of $H_2O_2$ by Merck's process and also as an air-purifier in submarines and mine-rescue apparatus. It is also employed to lower the moisture-content of closed spaces. It is used to prepare benzoyl peroxide, sodium perborate etc. As an oxidising agent, it is used in chemical analysis.

**Sodium Hydroxide** (NaOH) is an important heavy chemical and is used in large quantities in various industries. Its production is, therefore, always made on commercial scales and any laboratory method of preparation will be of academic interest only. For demonstration in a class, the material may be prepared in the following way :

A 10% solution of sodium carbonate is boiled with powdered quicklime (CaO). The mixture is well-stirred and more amounts of powdered quicklime are added till a filtered test portion is free from carbonate (tested with dilute mineral acid ; the presence of carbonate is indicated by effervescence). The mixture is then filtered and the filtrate evaporated to almost dryness, when crystals of sodium hydroxide are obtained : $Na_2CO_3 + CaO + H_2O = 2NaOH + CaCO_3 \downarrow$.

Pure sodium hydroxide may be prepared by the reaction of sodium amalgam with air-free distilled water. The solid product is obtained by evaporating the solution : $2Na/Hg + 2H_2O = 2NaOH + H_2 \uparrow + 2Hg \downarrow$.

**Properties** : A white, crystalline solid (m.p. 318°C), sodium hydroxide dissolves readily in water with the evolution of heat. (It is believed that the evolution of heat on dissolution is associated with the formation of the hydrates like $NaOH.H_2O$, $NaOH.2H_2O$ *etc.*) It is deliquescent and turns to a liquid on exposure to atmospheric air ; but, the resultant liquid is gradually transformed into solid sodium carbonate by the absorption of $CO_2$ from air. A dilute aqueous solution of sodium hydroxide is slippery to touch, and the strong solutions have corrosive action on skin. (It is, therefore, called *caustic soda.*) It is a strong base and precipitates hydroxides (or, in some cases, oxides) of many metals from solutions of their salts : $FeCl_3 + 3NaOH = Fe(OH)_3 \downarrow + 3NaCl$ ; $Al(NO_3)_3 + 3NaOH = Al(OH)_3 \downarrow + 3NaNO_3$ ; $CuCl_2 + 2NaOH = Cu(OH)_2 \downarrow + 2NaCl$ ; $ZnSO_4 + 2NaOH = Zn(OH)_2 \downarrow + Na_2SO_4$ ; $2AgNO_3 + 2NaOH = Ag_2O \downarrow + 2NaNO_3 + H_2O$ ; $HgCl_2 + 2NaOH = HgO \downarrow + 2NaCl + H_2O$. The hydroxides of the metals like

Zn, Al, Sn and Pb dissolve in excess of sodium hydroxide solution : $Zn(OH)_2+2NaOH=\underset{\text{Na-zincate}}{Na_2ZnO_2}+2H_2O$ ; $Al(OH)_3+NaOH=\underset{\text{Na-aluminate}}{NaAlO_2}+2H_2O$ ; $Sn(OH)_2+2NaOH=\underset{\text{Na-stannite}}{Na_2SnO_2}+2H_2O$ ; $Pb(OH)_2+2NaOH=\underset{\text{Na-plumbite}}{Na_2PbO_2}+2H_2O$.

The metals Zn, Al and Sn dissolve in concentrated solutions of sodium hydroxide to form soluble zincate, aluminate and stannate respectively, with the liberation of hydrogen : $Zn+2NaOH=Na_2ZnO_2+H_2$ ; $2Al+2NaOH+2H_2O=2NaAlO_2+3H_2$ ; $Sn+2NaOH+H_2O=Na_2SnO_3+2H_2$.

Fused sodium hydroxide attacks practically all metals ; the exceptions are Fe, Ni, Ag, Au and Pt. The amphoteric oxides of Zn, Al, Sn and Pb also react with concentrated sodium hydroxide solutions to give soluble salts : $ZnO+2NaOH=Na_2ZnO_2+H_2O$ ; $Al_2O_3+2NaOH=2NaAlO_2+H_2O$; $SnO_2+2NaOH=Na_2SnO_3+H_2O$; $PbO+2NaOH=Na_2PbO_2+H_2O$ ; $PbO_2+2NaOH=Na_2PbO_3+H_2O$.

When ammonium salts are heated with sodium hydroxide solution, ammonia is liberated : $NH_4X+NaOH=NaX+NH_3+H_2O$. ($X=Cl$, Br, I, $NO_3$, $\frac{1}{2}SO_4$ *etc.*)

Many non-metals react with sodium hydroxide. When white phosphorus is boiled with NaOH solution, phosphine is formed : $4P+3NaOH+3H_2O=PH_3\uparrow+3NaH_2PO_2$ (sod. hypophosphite). Chlorine, bromine and iodine react with NaOH solutions to give sodium halides and sodium hyphohalites or halates, according to the condition of the reaction : $Cl_2+2NaOH=NaCl+NaOCl+H_2O$ (with excess of cold and dil. NaOH soln.) ; $3Cl_2+6NaOH=5NaCl+NaClO_3+3H_2O$ (with excess of $Cl_2$ and at higher temperatures).

The acidic oxides of some non-metals combine with NaOH to form the sodium salts of the acids : $CO_2+2NaOH=Na_2CO_3+H_2O$ ; $SO_2+2NaOH=Na_2SO_3+H_2O$ ; $P_2O_5+6NaOH=2Na_3PO_4+3H_2O$.

Uses : Sodium hydroxide finds technical applications on a large scale. It is used in soap industry, dyestuff industry, rayon (*viscose*) industry, paper industry, cotton fabrics industry and petroleum industry (for refining). It is also used for the production of metallic sodium, for the purification of bauxite before extracting aluminium, for cleansing greased machine-parts and metal-sheets and also as a reagent in chemical laboratories.

**Manufacture of sodium hydroxide (caustic soda).**

(i) **From sodium carbonate by causticisation : Gossage's or LeBlanc's process.**—The double decomposition of $Na_2CO_3$ and $Ca(OH)_2$, resulting in the precipitation of $CaCO_3$ and formation of NaOH in solution, is taken advantage of in this process which is, however, not in much use now-a-days because of the availability of better electrolytic methods for obtaining caustic soda on a large scale. As the solubility of $Ca(OH)_2$ in the alkaline liquor rapidly decreases with the amount of NaOH formed, a 10-20% solution of $Na_2CO_3$ is generally causticised in a hemispherical iron vessel, in which wire-cages filled with quicklime are suspended. Steam is driven through the liquid to maintain it in boiling temperature, and a strong current of air is pumped at the bottom to ensure thorough agitation. The following reactions take place: $CaO+H_2O=Ca(OH)_2$ ; $Na_2CO_3+Ca(OH)_2=2NaOH+CaCO_3$. After boiling for a sufficient length of time, the liquid is allowed to settle, when $CaCO_3$ is thrown down as a precipitate. The clear supernatant liquid is siphoned off into multiple vacuum pans and evaporated, when crystals of NaOH are obtained. These are collected, melted and cast into sticks or beads.

(ii) **From sodium chloride through electrolysis** : When a concentrated aqueous solution of sodium chloride is electrolysed, $Na^+$ and $Cl^-$ are formed at the cathode and the anode respectively. Water of the solution is also electrolysed inspite of its small concentration, due to the fact that the deposition potential of $H^+$ ions is much lower than that of the $Na^+$ ions. The sodium ions, formed at the cathode, readily react with $OH^-$ ions in the system to produce sodium hydroxide, which accumulates in the neighbourhood of the cathode. The chlorine gas, liberated at the anode (in equivalent amount of the NaOH formed) diffuses through the medium and reacts with the alkali to form sodium hypochlorite and re-generate NaCl : $H_2O+e=\frac{1}{2}H_2+OH^-$ ; $NaCl \rightleftharpoons Na^++Cl^-$ ; $Na^++OH^-=NaOH$ ; $2Cl^--2e=Cl_2$ ; $2NaOH+Cl_2=NaCl+NaOCl+H_2O$. In order to obtain the desired product (NaOH), the diffusion of chlorine must be hindered. Various processes have been worked out for this purpose, of which **the Amalgam process** and **the Diaphragm process** are the most important ones.

(a) **The Amalgam process or the Castner-Kellner process** : This process is based on the fact that the deposition potential of the alkali metals is considerably lowered by amalgamation with mercury and, at the same time, the potential needed for the liberation of hydrogen is sufficiently raised due to the considerable overvoltage for the deposition of hydrogen on mercury. So, a concentrated solution of NaCl may be electrolysed in a cell with mercury cathode, and the sodium amalgam formed is decomposed by water to NaOH in a separate portion of the same cell or in a separate cell.

The commonly used cell is the *Castner-Kellner cell,* which is a rectangular iron vessel, divided into three compartments by two non-porous massive slate partitions which do not touch the bottom of the cell, but fit into grooves at the bottom. Two stout graphite electrodes project through the walls of the two outer compartments of the vessel and they act as the anodes. The middle compartment is fitted with an iron grid which serves as the cathode. A layer of mercury which is connected to the cathodes, covers the bottom of the vessel. The slate partitions, stated above, dip in this layer of mercury, without touching the bottom of the cell. A strong solution of sodium chloride is fed into the two outer compartments and water is fed into the central compartment. On passing electric current, sodium chloride is electrolysed, and $Cl_2$ is liberated at the anodes and escapes through the outlets (P,P). Sodium ions travel with the current and dissolve in the mercury to form sodium amalgam, after delivering their charges there.

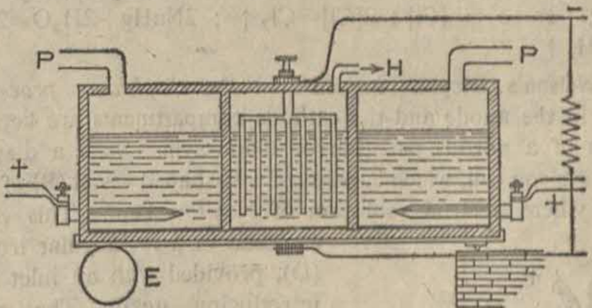

Fig. 11.3

A slow rocking motion is given to the whole apparatus by means of an eccentric wheel (E) placed on one side of the vessel. This causes the mercury layer to flow from the one compartment to the other and thus brings the amalgam in contact with water in the central compartment, when it decomposes to form NaOH and $H_2$, with the regeneration of mercury. The $H_2$ escapes through an outlet at the central compartment. When the NaOH formed in this compartment becomes sufficiently concentrated, it is run off to another vessel to evaporate to dryness. The dry mass is melted and cast into sticks, beads or lumps.

In some other form of the cell, (**Kellner-Solvay cell**), the rocking motion of the mercury layer is replaced by a flowing layer of it. Mercury is kept in a reservoir at a higher level at one side of the cell and it is allowed to flow very slowly over the slightly inclined bottom, to a collecting trough at the other end of the cell during the electrolysis. The sodium amalgam, collected at the trough, is subsequently decomposed by water in a secondary cell.

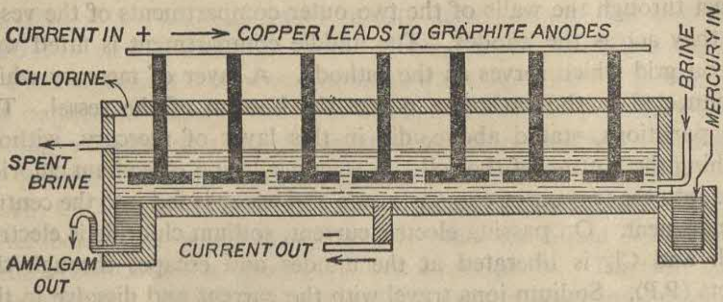

Fig. 11.4

$NaCl \rightleftharpoons Na^+ + Cl^-$ ; $Na^+ + e \rightarrow Na$ ; $Na + Hg \rightarrow NaHg$ (at the *cathode*) ; $Cl^- - e \rightarrow [Cl]$ ; $2[Cl] = Cl_2 \uparrow$ ; $2NaHg + 2H_2O = 2NaOH + 2Hg + H_2 \uparrow$ .

(b) **Nelson's Diaphragm Cell** : In the *diaphragm process*, the solutions in the anode and the cathode compartments are kept apart by means of a porous partition or diaphragm. Such a diaphragm cell is the Nelson cell, which consists of a U-shaped vessel (B) of porous asbestos, where a strong solution of NaCl is kept. This vessel is enclosed in a rectangular iron tank (D), provided with an inlet (F) for introducing steam. The graphite anode (A) is placed in the vessel(B) which has two pipes (E and G), one for the feeding of NaCl solution and the other for the escape of $Cl_2$ gas. Very close to the outer surface of the U-shaped vessel is placed the cathode which consists of perforated iron sheet or iron wire-gauge (C). A typical unit of such a cell is shown in fig. 11.5, a number of which is actually used in a series in commercial operation. The solution of NaCl, kept in the vessel (B), slowly

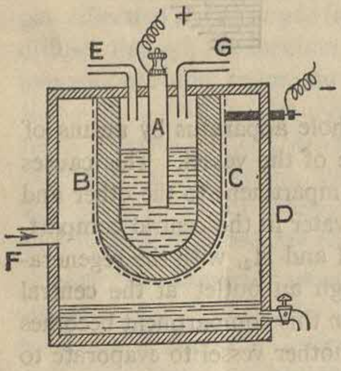

Fig. 11.5

diffuses through its porous wall and reaches the cathode, when it suffers electrolytic decomposition. $Cl_2$ is liberated at the anode and passes out through the outlet (G), while the metallic sodium, liberated at the cathode is acted upon by the steam injected through (F) and forms NaOH. (The hydrogen liberated in this reaction is led out of the tank through an outlet, which is not shown in the figure.) Steam dissolves the NaOH to form a solution which is tapped off from time to time for working up the solid product. It also serves to wash out the clogging of the porous asbestos wall by solid NaOH.

The main disadvantage of this process is the high electrical resistances offered by the diaphragms towards the passage of current. The product obtained in this process is also contaminated with unchanged NaCl.

**Sodium chloride** or *Common salt* **(NaCl)** : Large deposits of sodium chloride, in the form of **Rock salt,** are found in many parts of the world. Enormous quantities of the salt also exist in the water of oceans and seas, which is due to the continuous lixivation of soluble salts of the land by the water of rain and rivers flowing to the oceans for many geological ages. Sodium chloride is obtained from rock salt by breaking it down from mines and pulverising in grinding mills. In certain cases, it is the practice to leach the rock salt with water to prepare a saturated solution of brine and evaporate the solution to crystallise out sodium chloride. In countries where abundant sunshine is available, sodium chloride is obtained on a large scale by solar evaporation of sea-water at the sea-shores. Shallow open tanks are erected on flat land at the sea-shore, in which saline sea-water is filled. The water is gradually evaporated by sunshine and wind and solid sodium chloride settle at the bottom of the tanks and is removed by perforated shovels and dried. In countries where sunshine is not adequate, sodium chloride is obtained from sea-water by the **freezing technique,** in which the water is frozen, when *only* pure water solidifies, leaving the mother-liquor more concentrated with respect to the salts. Ice is removed and the mother-liquor is evaporated to obtain the solid salt. Sodium chloride manufactured from sea-water contains many impurities such as $MgCl_2$, $CaCl_2$, $CaSO_4$, $Na_2SO_4$ *etc.* [The presence of $MgCl_2$ in common salt is responsible for its dissolution in moist weather.]

Pure sodium chloride may be obtained by passing HCl gas or adding conc. HCl to a saturated and filtered solution of sodium chloride, when perfectly white, pure NaCl is precipitated due to the *common-ion effect.* It is filtered and washed with pure hydrochloric acid and dried by heating.

Sodium chloride forms colourless, transparent cubic crystals, melting at 820°C. It is soluble in water. On heating with conc. $H_2SO_4$, it liberates hydrogen chloride : $NaCl+H_2SO_4=NaHSO_4+HCl$ ; $NaHSO_4+NaCl=Na_2SO_4+HCl$. A mixture of NaCl and $MnO_2$ liberates chlorine on heating with conc. $H_2SO_4$ : $2NaCl+MnO_2+3H_2SO_4=MnSO_4+2NaHSO_4+Cl_2+2H_2O$. A concentrated ammoniacal solution of NaCl precipitates sodium bicarbonate on passing a stream of $CO_2$ through it : $NaCl+NH_4OH+CO_2=NaHCO_3+NH_4Cl$.

Sodium chloride is a constituent of food and it is also used for the preservation of meat, fish *etc.* It is the starting material for the manufacture of sodium metal, chlorine, caustic soda, sodium carbonate, sodium sulphate *etc.* Its important applications also include the glazing of earthen wares, salting out of soap during its manufacture, re-generation of water-softeners and making of freezing-mixtures.

**Sodamide** ($NaNH_2$) is prepared by passing dry ammonia gas over sodium heated at 190°—200°C : $2Na+2NH_3=2NaNH_2+H_2\uparrow$. It is a white solid (m.p. 210°C) and is decomposed by water into NaOH and $NH_3$ : $NaNH_2+H_2O=NaOH+NH_3$. Sodamide is largely used in organic synthesis.

**Sodium nitrate** ($NaNO_3$) is found as **Chile saltpetre** or **Caliche** deposits in Peru, Chile and Bolivia. The natural deposits contain about 65% $NaNO_3$, and the salt is recovered from it by extraction with water and fractional crystallisation.

A white, deliquescent and crystalline solid, sodium nitrate melts at 316°C and is extremely soluble in water. It becomes moist or even dissolves by the water vapour absorbed from air. It decomposes into sodium nitrite and oxygen on strong heating : $2NaNO_3=2NaNO_2+O_2$. When boiled with conc. $H_2SO_4$, it produces nitric acid : $2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3$.

Sodium nitrate is used as a fertilizer. It is also the starting material for the manufacture of nitric acid, sodium nitrite and potassium nitrate.

**Sodium nitrite** ($NaNO_2$) is obtained by strongly heating $NaNO_3$, either alone or with metals like lead or copper : $2NaNO_3=2NaNO_2+O_2\uparrow$ ; $NaNO_3+Pb=NaNO_2+PbO$. If the salt is prepared by the second reaction, the resultant $NaNO_2$ is extracted with water and isolated as crystals by concentrating the water-extract. It is manufactured by passing a mixture of NO and $NO_2$ (obtained by the oxidation of ammonia) into a solution of sodium carbonate or sodium hydroxide : $Na_2CO_3+NO+NO_2=2NaNO_2+CO_2$ ; $2NaOH+NO+NO_2=2NaNO_2+H_2O$.

Sodium nitrite forms colourless crystals (m.p. 284°C), slightly deliquescent and highly soluble in water. It acts both as an oxidising and a reducing agent. It oxidises stannous chloride to stannic chloride, potassium iodide to iodine in acidic solution and bleaches indigo by oxidation.

$$SnCl_2+2NaNO_2+4HCl=SnCl_4+2NaCl+2H_2O+2NO.$$

$$2KI+2NaNO_2+4HCl=I_2+2NaCl+2KCl+2H_2O+2NO.$$

On the other hand, it reduces $KMnO_4$ and $K_2Cr_2O_7$ solutions.

$$2KMnO_4+3H_2SO_4+5NaNO_2=K_2SO_4+2MnSO_4+5NaNO_3+3H_2O.$$

$$K_2Cr_2O_7+8HCl+3NaNO_2=2CrCl_3+2KCl+3NaNO_3+4H_2O.$$

When sodium nitrite is boiled with a solution of $NH_4Cl$ or with an acidic solution of urea, it is decomposed to evolve nitrogen gas :

$$NaNO_2+NH_4Cl=NaCl+2H_2O+N_2\uparrow\ ;$$

$$2NaNO_2+CO(NH_2)_2+2HCl=2NaCl+CO_2+3H_2O+2N_2\uparrow.$$

Sodium nitrite is used in diazotisation reaction and to manufacture azo-dyes.

**Sodium sulphide** ($Na_2S.9H_2O$) is prepared on a large scale by heating (reducing) salt-cake (crude $Na_2SO_4$) with half its weight of coke in a reverberatory furnace for about 2 hours : $Na_2SO_4+4C=Na_2S+4CO$. The molten mass from the furnace is taken out, cooled and leached with water to dissolve out $Na_2S$ from the mass. The clear filtrate gives colourless crystals of $Na_2S.9H_2O$ on concentration.

Sodium sulphide is a deliquescent substance and its aqueous solution is highly alkaline due to hydrolysis :

$$Na_2S+H_2O \rightleftharpoons NaSH+NaOH.$$

It is used for manufacturing sulphur-dyes and in the tanning industry to remove hair from hides.

**Sodium bisulphite ($NaHSO_3$) and metabisulphite ($Na_2S_2O_5$) :**

Sodium bisulphite is formed in solution on saturating an aqueous solution of sodium carbonate with $SO_2$ gas. The excess of $SO_2$ is removed by evaporation and the solution is dried, when sodium metabisulphite ($Na_2S_2O_5$ or $Na_2SO_3.SO_2$) is obtained in the solid state.

$$Na_2CO_3+H_2O+2SO_2=2NaHSO_3+CO_2\ ;$$

$$2NaHSO_3+SO_2=Na_2S_2O_5+H_2SO_3.$$

Sodium metabisulphite can also be prepared by passing $SO_2$ gas over dry sodium carbonate.

Sodium metabisulphite decomposes on heating to form sodium sulphite and sulphur dioxide. So, it acts as a strong reducing agent :

$$Na_2S_2O_5=Na_2SO_3+SO_2.$$

Sodium metabisulphite is used in photography and also to remove excess chlorine from cloth and paper bleached by chlorine. It is also used as a food-preservative and as a germicide.

**Sodium sulphite ($Na_2SO_3$)** : Sodium bisulphite is first prepared by any one of the methods detailed above. When a boiling aqueous solution of sodium bisulphite is neutralized with sodium carbonate, sodium sulphite is formed in solution. The resultant solution is crystallised above 22°C to obtain anhydrous crystals of sodium sulphite. (Crystallisation below 22°C produces the hydrated salt, $Na_2SO_3.H_2O$.)

Sodium sulphite is a white crystalline salt. It is decomposed by dilute mineral acids with the evolution of sulphur dioxide :

$$Na_2SO_3+2HCl=2NaCl+SO_2+H_2O.$$

It is used as a mild reducing agent.

**Sodium sulphate ($Na_2SO_4$)** : This salt is formed as a by-product (along with sodium bisulphate, $NaHSO_4$) during the manufacture of $HNO_3$ from sodium nitrate and conc. $H_2SO_4$. As *salt cake* (impure $Na_2SO_4$), it is produced in the Le Blanc process of the manufacture of sodium carbonate. The salt-cake is extracted with water and the Glauber's salt ($Na_2SO_4.10H_2O$) is obtained from the extract by cooling it below 32.38°C. At higher temperatures, the less soluble anhydrous $Na_2SO_4$ separates out. The decahydrate effloresces in air to form the anhydrous salt. It is also prepared by passing a mixture of $SO_2$, air and water-vapour over heated sodium chloride (**Hargreave's process**) : $4NaCl+2SO_2+2H_2O+O_2(air)=2Na_2SO_4+4HCl$. Sodium sulphate is available in three forms, *viz.* the decahydrate or Glauber's salt ($Na_2SO_4.10H_2O$), the hepta-hydrate ($Na_2SO_4.7H_2O$) and the anhydrous variety ($Na_2SO_4$).

Sodium sulphate is a white, crystalline solid, soluble in water. The solubility of the salt in water increases with temperature upto 32.38°C and then it falls. [At 32.38°C, the solid is present as $Na_2SO_4.10H_2O$ ; above this temperature, the decahydrate changes to the anhydrous variety which is less soluble in water and hence, the decrease of solubility.] When strongly heated with carbon, sodium sulphate is reduced to sodium sulphide : $Na_2SO_4+4C=Na_2S+4CO\uparrow$.

The salt is used in the manufacture of glass. Impure $Na_2SO_4$ (*salt cake*) is used for the manufacture of sodium carbonate and for making craft paper. The salt is used as medicine. Anhydrous $Na_2SO_4$ is used as a desiccating agent.

**Sodium bisulphate (Sodium hydrogen sulphate, $NaHSO_4$)** is formed on heating anhydrous $Na_2SO_4$ with conc. $H_2SO_4$ : $Na_2SO_4+H_2SO_4$

$=2NaHSO_4$. The salt can also be prepared by the reaction between equimolecular proportions of NaOH and $H_2SO_4$ : $NaOH+H_2SO_4=NaHSO_4+H_2O$. As a by-product, it is formed along with $Na_2SO_4$ during the manufacture of $HNO_3$ from saltpetre and sulphuric acid.

Sodium bisulphate is a water-soluble, white crystalline substance, melting at 182°C. The aqueous solution of the salt is highly acidic due to the dissociation : $NaHSO_4 \rightleftharpoons Na^+ + HSO_4^-$ ; $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$. The solid salt forms sodium pyrosulphate on heating : $2NaHSO_4=Na_2S_2O_7+H_2O$.

Sodium bisulphate is used for cleaning iron-sheets before tinning.

**Sodium thiosulphate ($Na_2S_2O_3$) :** The salt generally exists as a hydrated species with 5 molecules of water of crystallisation ($Na_2S_2O_3.5H_2O$) which is commercially known as **hypo.**

**Preparation :** (i) Powdered sulphur is added gradually to a boiling solution of sodium sulphite with constant stirring, till the alkalinity of the solution disappears. When no more sulphur is dissolved, the hot mixture is filtered and the clear filtrate is concentrated by heat. On cooling the concentrated solution, practically colourless hydrated crystals of $Na_2S_2O_3.5H_2O$ are obtained. These are collected by filtration and dried in air.

$$Na_2SO_3+S=Na_2S_2O_3.$$

[The solution of sodium sulphite, used in the above preparation of sodium thiosulphate, is obtained in the following way :

A saturated aqueous solution of $Na_2CO_3$ is prepared. One half of the volume of this solution is saturated by passing $SO_2$ gas through it. The other half of the solution is added to the one saturated with $SO_2$, when a solution of sodium sulphite is obtained :

$$Na_2CO_3+2SO_2+H_2O=2NaHSO_3+CO_2\ ;$$
$$2NaHSO_3+Na_2CO_3=2Na_2SO_3+H_2O+CO_2.]$$

(ii) Sodium thiosulphate is also formed on boiling sulphur-powder with a solution of sodium hydroxide. (Some amount of sodium sulphide is also formed in this process.) When excess of sulphur is used, sodium polysulphides (e.g. $Na_2S_5$) are also formed.

The sulphide and polysulphides of sodium, formed in the process, are converted into sodium thiosulphate by aerial oxidation.

$$6NaOH+4S=Na_2S_2O_3+2Na_2S+3H_2O\ ;$$
$$2Na_2S+H_2O+2O_2=Na_2S_2O_3+2NaOH\ ;$$
$$2Na_2S_5+3O_2=2Na_2S_2O_3+6S.$$

(iii) Sodium thiosulphate can also be prepared by the **Spring's reaction** which is carried but by treating a mixture of sodium sulphide and sodium sulphite with iodine :

$$Na_2S+Na_2SO_3+I_2=Na_2S_2O_3+2NaI.$$

On crystallising the resultant solution, the less soluble $Na_2S_2O_3.5H_2O$ first crystallises out.

(iv) When $SO_2$ gas is passed through a solution of sodium sulphide, sodoium thiosulphate is formed.

$$2Na_2S+3SO_2=2Na_2S_2O_3+S.$$

The resultant mixture is filtered and the filtrate is evaporated to crystallisation.

(v) **Manufacture of $Na_2S_2O_3.5H_2O$ :** Sodium thiosulphate is generally manufactured from the spent mother-liquor of the Le Blanc process of manufacturing sodium sulphate. This mother-liquor contains sodium sulphide, sodium carbonate, sodium sulphite and sodium sulphate. This solution is concentrated by boiling and $SO_2$ gas is then passed through it. As a result, sodium thiosulphate is formed in solution. The solution is filtered and then concentrated by heating to crystallisation, when almost colourless crystals of $Na_2S_2O_3.5H_2O$ are obtained.

$$Na_2SO_3+2Na_2S+3SO_2=3Na_2S_2O_3\ ;$$
$$Na_2CO_3+2Na_2S+4SO_2=3Na_2S_2O_3+CO_2.$$

**Properties :** Sodium thiosulphate forms almost colourless hydrated crystals with 5 molecules of water of crystallisation. These hydrated crystals are efflorescent. The hydrated salt leaves the water of crystallisation completely on heating at 215°C. The substance is highly soluble in water and it has a tendency to form super-saturated solution.

Sodium thiosulphate decomposes on heating with the formation of $SO_2$, $H_2S$ and S. On reacting with dilute mineral acids, it dissolves with the evolution of $SO_2$ and precipitation of sulphur :

$$Na_2S_2O_3+2HCl=2NaCl+SO_2+S+H_2O.$$

*Reaction with halogens* : Chlorine oxidises sodium thiosulphate to sodium sulphate, with the separation of sulphur : $Na_2S_2O_3+Cl_2+H_2O=Na_2SO_4+S+2HCl$. But, iodine oxidises it to sodium tetrathionate :

$$2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI.$$

*Reaction with barium chloride* : A fairly concentrated solution of sodium thiosulphate reacts with barium chloride solution to form a white precipitate of barium thiosulphate ;

$$BaCl_2+Na_2S_2O_3=BaS_2O_3\downarrow+2NaCl.$$

But, as calcium thiosulphate is quite soluble in water, no such precipitate is formed when sodium thiosulphate solution is added to a solution of calcium chloride.

*Reaction with silver halide* : The insoluble silver halides dissolve in sodium thiosulphate solution with the formation of the complex salt, sodium argentothiosulphate :

$$AgBr+2Na_2S_2O_3=\underset{\text{Sodium argento-thiosulphate}}{Na_3[Ag(S_2O_3)_2]}+NaBr.$$

This reaction is employed in photography.

*Reaction with silver nitrate* : When a very dilute solution of sodium thiosulphate is added to a solution of silver nitrate, an unstable white precipitate of $Ag_2S_2O_3$ is formed. But, the precipitate immediately changes colour through yellow, brown and ultimately to black. The black substance is silver sulphide.

$$2AgNO_3+Na_2S_2O_3=Ag_2S_2O_3+2NaNO_3\ ;$$

$$Ag_2S_2O_3+H_2O=Ag_2S+H_2SO_4.$$

But, a fairly concentrated solution of sodium thiosulphate does not practically form any precipitate with $AgNO_3$ solution. The silver thiosulphate that is formed instantaneously reacts with excess of sodium thiosulphate to form the soluble complex salt, sodium argento-thiosulphate.

$$Ag_2S_2O_3+3Na_2S_2O_3=2Na_3[Ag(S_2O_3)_2]$$

*Reaction with gold (auric) salt* : At the first step of the reaction, an auric salt is reduced to the aurous state by sodium thiosulphate. The resultant aurous salt then reacts with excess of sodium thiosulphate solution to form soluble complex salt, sodium aurothiosulphate.

$$AuCl_3+2Na_2S_2O_3=AuCl+Na_2S_4O_6+2NaCl\ ;$$

$$AuCl+2Na_2S_2O_3=\underset{\text{Sodium auro-thiosulphate.}}{Na_3[Au(S_2O_3)_2]}+NaCl$$

*Reaction with cupric salts* : Sodium thiosulphate at first reduces cupric salt to the cuprous state. The resultant cuprous salt dissolves in excess of sodium thiosulphate solution, with the formation of complex salt :

$$2CuCl_2+2Na_2S_2O_3=2CuCl+Na_2S_4O_6+2NaCl\ ;$$

$$2CuCl+Na_2S_2O_3=Cu_2S_2O_3+2NaCl\ ;$$

$$3Cu_2S_2O_3+2Na_2S_2O_3=Na_4[Cu_6(S_2O_3)_5].$$

*Reaction with ferric chloride* : When a few drops of ferric chloride solution are added to a solution of sodium thiosulphate, a violet solution of ferric thiosulphate is formed : $2FeCl_3+3Na_2S_2O_3 \rightleftharpoons Fe_2(S_2O_3)_3+6NaCl$. But, as the ferric salt is reduced to the ferrous state by sodium thiosulphate, the violet colour soon disappears.

**Uses of sodium thiosulphate** : Sodium thiosulphate is used in photography. It is also used in the extraction of gold and silver. It is an important reagent in volumetric analysis. It is also used in medicine.

**Sodium carbonate** ($Na_2CO_3$) : Natural deposits of sodium carbonate occur at some drying lakes of East Africa and Egypt. It is an important industrial chemical and as such, it is always prepared on a manufacturing scale. In a laboratory preparation, which is only of academic interest, the compound may be obtained by passing $CO_2$ into a saturated solution of caustic soda, till the requisite increase in weight of the reaction-mixture takes place. The mixture, on standing, deposits crystals of $Na_2CO_3.10H_2O$ : $2NaOH+CO_2=Na_2CO_3+H_2O$. The anhydrous salt may be obtained by heating the dry decahydrate, or better by the thermal decomposition of sodium bicarbonate : $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$.

**Manufacture of Sodium Carbonate :** Three processes are available for the preparation of sodium carbonate on a large scale. These are : (i) **the Le Blanc process,** (ii) **the Ammonia-Soda or Solvay process** and (iii) **the electrolytic process.**

(i) The **Le Blanc process** is the oldest one, but it is now practically obsolete for the production of sodium carbonate. [At present, this process is mainly used for the industrial preparation of sodium sulphate and some potassium carbonate.]

In the first stage of the Le Blanc process, salt-cake or crude sodium sulphate is prepared by heating sodium chloride and conc. $H_2SO_4$ (in 2 : 1 molecular proportion) on a cast-iron pan placed at one side of the furnace (Fig. 11.6). The temperature is so controlled that sodium bisulphate is formed here as a pasty mass. The solidifying mass of $NaHSO_4$ is then pushed into the hearth of the furnace, where it is subjected to higher temperature to yield sodium sulphate. HCl gas, formed in the process, is absorbed in water in the absorption tower to produce hydrochloric acid of commerce : $NaCl + H_2SO_4 = NaHSO_4 + HCl \uparrow$ ; $NaHSO_4 + NaCl = Na_2SO_4 + HCl \uparrow$ .

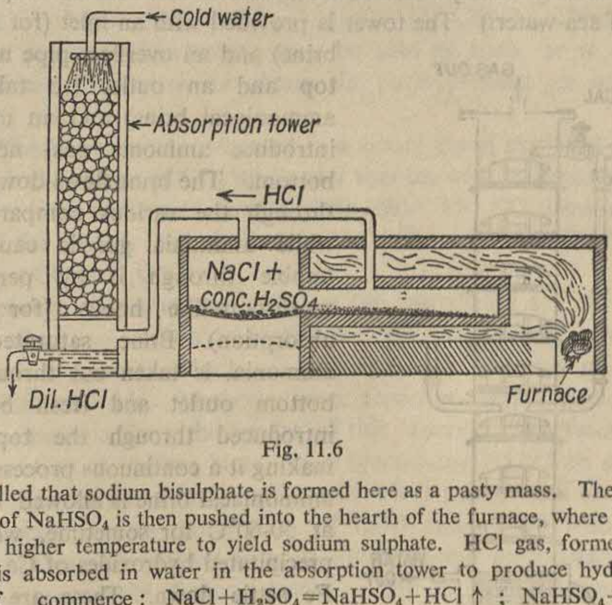

Fig. 11.6

The cooled solid lumps of $Na_2SO_4$ **(salt cake)** are broken up into coarse granules, mixed with powdered limestone and coal-dust and heated at about 1000°C in a rotary furnace, when sodium sulphate is reduced to sodium sulphide, which reacts with limestone to form sodium carbonate and calcium sulphide :

$$Na_2SO_4 + 2C = Na_2S + 2CO_2 \; ; \; Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

The blackish product is called **Black-ash** and it contains about 45% $Na_2CO_3$.

Powdered black-ash is then lixivated or extracted with water in large iron-tanks, when $Na_2CO_3$ goes into solution. The clear solution is siphoned off and evaporated to obtain the crystals of $Na_2CO_3.10H_2O$, which may be heated to [illegible] hydrous salt.

(ii) **The Ammonia-Soda or Solvay process :** Large amounts of sodium carbonate are manufactured at present by this process. It produces $Na_2CO_3$ in a higher state of purity and at a much lower cost than the Le Blanc process. The fundamental reaction on which this process depends is expressed by the equation : $NaCl + (NH_4)HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl$. The sparing solubility of $NaHCO_3$ in the saline medium results in its precipitation and thus, drives the equilibrium much towards the right-hand side, so that better yield of the product is obtained.

During the operational procedure of the process, **ammoniacal brine** is first prepared by saturating *brine* (a concentrated solution of NaCl) with ammonia gas at 70°C in an iron tower, provided with shelves. [The brine is generally obtained from natural salt-beds or evaporating tanks of sea-water.] The tower is provided with an inlet (for feeding brine) and an overflow pipe near the top and an outlet (to take out ammoniacal brine) and an inlet (to introduce ammonia gas) near the bottom. The brine flows downwards through the various compartments, while ammonia gas is caused to bubble through it by perforated mushroom-like hoods (for better absorption). Brine, saturated with ammonia, is taken out through the bottom outlet and fresh brine is introduced through the top, thus making it a continuous process. The ammoniacal brine is allowed to stand at 50-60°C for sometime, when the precipitated hydroxides of Ca, Mg or Fe settle down. These are filtered and the clear solution at 30°C is pumped into the *carbonating tower* for *carbonation*.

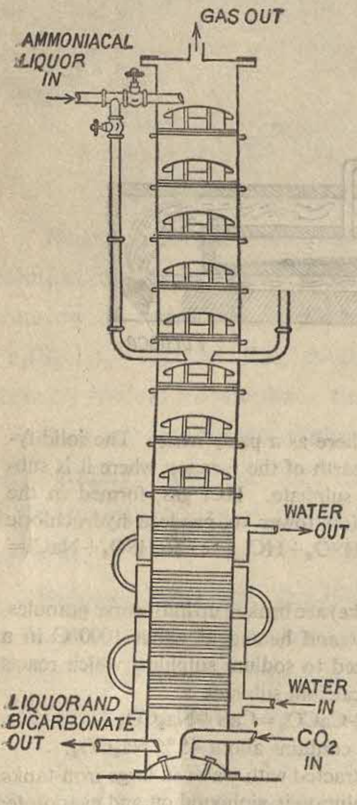

Fig. 11.7

The **carbonating** or **Solvay tower** is a long cylindrical iron tower, divided inside into a number of horizontal compartments by iron-shelves. Each shelf has a central hole covered with a perforated hood (Fig. 11.7). Ammoniacal brine is introduced into the tower through an inlet near the top. Carbon dioxide is prepared in a near-by lime-kiln, and the washed gas is compressed to about 2—5 atmospheric pressure and passed into the tower through an inlet near its bottom. The gas is divided into very fine bubbles on passing through the perforated hoods and meets the descending liquid in a counter-current manner, causing perfect absorption thereby. The absorption results in the evolution of considerable quantity of heat, and in order to keep down the temperature of the liquor, the lower portion of the tower is fitted with cooling tubes through which cold water is circulated. Sodium bicarbonate is formed during the absorption of $CO_2$ by the ammoniacal liquor and is precipitated as solid on the shelves within the tower. The pasty suspension of $NaHCO_3$ is taken out, filtered by suction and dried. The following reactions occur within the tower : $NH_3+CO_2+H_2O=(NH_4)HCO_3$ ; $NaCl+(NH_4)HCO_3=NaHCO_3+NH_4Cl$. [Sodium bicarbonate may be sold as such, or it may be recrystallised from water to obtain the purer product for medicinal use.]

Sodium bicarbonate is heated in a closed vessel provided with an outlet for the escape of $CO_2$ and water vapour, when it decomposes to give anhydrous sodium carbonate (**Soda ash**). The $CO_2$ liberated may be used for further carbonation in the Solvay tower : $2NaHCO_3=Na_2CO_3+CO_2+H_2O$.

**Recovery of ammonia** : Among the ingredients for the manufacture of sodium carbonate by the Solvay process, only ammonia is somewhat expensive. Much of ammonia is lost in this process as ammonium chloride. Methods have, therefore, been developed to recover ammonia from the wastes of this process. The filtrate after the separation of sodium bicarbonate (containing $NH_4Cl$ in solution) is transferred to the recovery stills, where it is mixed with lime (from the lime-kiln for the production of $CO_2$) and boiled with steam. The ammonia gas evolved is used for preparing ammoniacal brine for feeding to the Solvay tower : $2NH_4Cl+Ca(OH)_2=CaCl_2+2NH_3+2H_2O$.

(iii) **Electrolytic process** : Sodium carbonate is also manufactured by an electrolytic process by electrolysing a strong solution of sodium chloride and passing $CO_2$ at the same time into the electrolytic cell. It is generally carried out in a diaphragm cell (**Hargreaves-Bird cell**), which is a rectangular iron box of three compartments made by porous asbestos sheets (diaphragms). A gas-carbon anode is placed in the central compartment in which the electrolyte (brine) is introduced through an inlet near the bottom. On the outer surface of the diaphragms are tightly pressed perforated copper sheets or wire-gauge which act as cathodes. The electrolyte solution slowly oozes out through the porous diaphragm and is electrolysed. Steam and $CO_2$ are simultaneously introduced in the cell through two openings near its bottom. During electrolysis, sodium metal is liberated at the cathode and it is at once acted upon by steam to form NaOH and $H_2$. Hydrogen escapes through outlets at the top. The NaOH formed, immediately reacts with $CO_2$ to form sodium carbonate, which dissolves in water of the condensed steam. Solution of sodium carbonate is taken out through openings at the base and evaporated to obtain crystals of $Na_2CO_3.10H_2O$. The waste liquor of electrolysis is removed through an opening near the top of the cell. The product is about 98% pure.

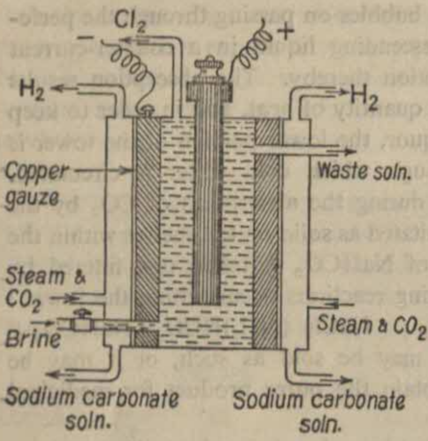

Fig. 11.8

**Properties** : Sodium carbonate crystals exist as the decahydrate ($Na_2CO_3.10H_2O$), the monohydrate ($Na_2CO_3.H_2O$) or the anhydrous salt ($Na_2CO_3$). The decahydrate loses water molecules, when exposed to air, to give the monohydrate. The anhydrous salt (**Soda ash**) is obtained on heating the monohydrate or the decahydrate. The anhydrous or the monohydrated salt form the decahydrate when crystallised from water at ordinary temperatures. A white crystalline solid, sodium carbonate is soluble in water. The aqueous solution is strongly alkaline due to hydrolysis : $Na_2CO_3+2H_2O \rightleftharpoons 2NaOH+H_2CO_3$. As a result, an aqueous solution of sodium carbonate precipitates $Al(OH)_3$ and $Fe(OH)_3$ from aqueous solutions of aluminium and ferric salts. A strong solution of the salt absorbs $CO_2$ from air, and sparingly soluble sodium bicarbonate is precipitated : $Na_2CO_3+H_2O+CO_2=2NaHCO_3$.

Sodium carbonate melts at 854°C without decomposition. Like other metallic carbonates, it is decomposed by dilute mineral acids with effervescence of $CO_2$ : $Na_2CO_3+2HCl=2NaCl+CO_2+H_2O$. A solution of sodium carbonate is transformed into sodium hydroxide on boiling with lime (*causticisation*) : $Na_2CO_3+Ca(OH)_2=2NaOH+CaCO_3\downarrow$.

Sodium carbonate is widely used in the soap, glass and caustic soda industries. It has ample use for washing purposes, for softening hard water and as a laboratory reagent.

**Sodium bicarbonate ($NaHCO_3$)** is obtained, as we have seen, as an intermediate in the Solvay process of manufacture of sodium carbonate. It may also be obtained by passing a stream of $CO_2$ gas into a saturated solution of sodium carbonate, when the less soluble sodium bicarbonate precipitates out. It is filtered, washed with cold water and dried.

Sodium bicarbonate is a white crystalline solid. It is sparingly soluble in cold water, but more soluble in hot water. In aqueous solution, the hydrolysis : $HCO_3^- + H_2O \rightleftharpoons OH^- + H_2CO_3$, occurs to a small extent and, as such, an aqueous solution of the salt is slightly alkaline. The solid salt as well as its aqueous solution decompose on heating : $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$.

Sodium bicarbonate is used as an *antacid* in medicine. It is also a constituent of *baking powder*.

**Sodium cyanide (NaCN)** is prepared by heating a mixture of metallic sodium and charcoal powder in an atmosphere of ammonia gas in a closed furnace. Sodamide is first formed, which reacts with charcoal powder to produce sodium cyanide, through the intermediate formation of sodium cyanamide ($Na_2NCN$) :

$$2NH_3 + 2Na = 2NaNH_2 + H_2 \; ; \; 2NaNH_2 + C = Na_2N.CN + 2H_2 \; ;$$
$$Na_2N.CN + C = 2NaCN.$$

The molten sodium cyanide is run off and cast into solid.

Sodium cyanide is also obtained by heating a mixture of sodium carbonate and powdered coke in a stream of nitrogen gas in the presence of finely divided iron powder as catalyst : $Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO$. Sodium cyanide is also obtained from sodium ferrocyanide $Na_4[Fe(CN)_6]$, a by-product in coal-gas industry, which is formed while passing coal-gas through alkaline ferrous sulphate solution to remove HCN from the gas. When solid sodium ferrocyanide is heated with metallic sodium in a covered iron-crucible, sodium cyanide results : $Na_4[Fe(CN)_6] + 2Na = 6NaCN + Fe$. The fused mass is cooled, extracted with water and the water-extract is evaporated to get solid sodium cyanide.

Sodium cyanide is a white solid with characteristic smell. It is soluble in water and is hydrolysed in aqueous solution, so that the solution reacts alkaline : $NaCN + H_2O \rightleftharpoons NaOH + HCN$.

Sodium cyanide is used in electroplating, in the extraction of gold and silver and also in organic synthesis.

**Sodium azide ($NaN_3$) :** Sodium azide is prepared by heating sodamide in a stream of nitrous oxide : $NaNH_2 + N_2O = NaN_3 + H_2O$.

Sodium azide is a white substance which decomposes into sodium and nitrogen on strong heating : $2NaN_3 = 2Na + 3N_2$. An aqueous solution of sodium azide reacts with carbon disulphide to form sodium azidodithio-carbonate : $NaN_3 + CS_2 = NaS.CS.N_3$.

**Tests :** (i) Sodium salts gives a strong golden yellow flame in the *flame test*. The yellow colour of the flame looks colourless when viewed through blue coloured glass. (ii) Sodium salt solutions form a yellow crystalline precipitate with a solution of zinc uranyl acetate in acetic acid.

Sodium is estimated by weighing as anhydrous $Na_2SO_4$ or as sodium zinc uranyl acetate.

## POTASSIUM

*Symbol* : K ; *Atomic No.*=19 ; *Atomic wt.*=39·1
*Electronic Configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$.
[First isolated by Davy (1807)]

**Occurrence :** Potassium does not occur free in nature due to its highly reactive nature. Compounds of potassium are, however, widely distributed in nature, indeed in small quantities. In *mica* and *felspar*, the metal occurs as *silicate*. The chief source of potassium is the deposits at Stassfurt (Germany). They contain (i) *Carnallite* (KCl, $MgCl_2$, $6H_2O$), (ii) *Polyhalite*, ($K_2SO_4$, $MgSO_4$, $2CaSO_4$, $2H_2O$) and (iii) *Kainite* (KCl, $MgSO_4$, $3H_2O$). The metal also occurs as chloride in *sylvine*. Water of the Dead Sea (Palestine) and some drying lakes near Tunis and California contain large quantities of potassium chloride. As *Saltpetre* or *nitre* ($KNO_3$), the metal occurs in some dry districts of Northern India. In the plant kingdom, potassium occurs as the salts of organic acids, so that the metal is left in the ashes as potassium carbonate (Potash), when the dried plants are burnt. Potassium is also found in very small quantities in some animal products, such as blood serum, sweats of certain animals *etc*.

**Extraction :** Production of potassium is generally made on a relatively small scale, since this metal offers no technical advantage over sodium. Potassium is extracted in a way similar to sodium, by electrolysing fused potassium hydroxide (*caustic potash*). In this process, however, a part of the metal liberated remains dissolved in the fused electrolyte. The extraction is also made by electrolysing fused KCl (mixed with a little potassium fluoride to lower the melting point of KCl).

**Properties :** Potassium is silver-white, soft metal of sp. gr. 0.86 (m.p. 63.6°C). It readily tarnishes when exposed to air. It is a good conductor ot heat and electricity. In chemical properties, it is very similar to sodium, but is more reactive. It reacts with water, more energetically than sodium, with the liberation of hydrogen which catches fire and burns with a lilac (violet) flame, due to the emission of energy by the excited gaseous atoms. On heating in excess of air, potassium yields the superoxide, $KO_2$.

Potassium is used for the preparation of potassium cyanide and as a condensing agent in organic synthesis. Potassium amalgam is a good reducing agent. An alloy of sodium and potassium (liquid) is used in high-temperature thermometres.

## COMPOUNDS OF POTASSIUM.

**Potassium Hydride, KH,** is a saline hydride like NaH, and is prepared analogously by heating the metal in dry hydrogen. It resembles the sodium compound in properties.

**Potassium Monoxide** ($K_2O$) is formed when potassium is heated at 185°C in a limited supply of air or oxygen. The excess of the unconverted metal is removed by distillation in vacuo. It is also produced by heating potassium nitrate with metallic potassium,

$$2KNO_3+10K=6K_2O+N_2$$

Potassium monoxide in a white solid, turning yellow when heated. As a basic oxide, it dissolves in water to form potassium hydroxide :

$$K_2O+H_2O=2KOH.$$

**Potassium Superoxide** ($KO_2$) is formed when potassium is burnt in excess of air or oxygen : $K+O_2=KO_2$. It is a bright yellow powder. With cold water, it forms potassium hydroxide, $H_2O_2$ and oxygen : $2KO_2+2H_2O=2KOH+H_2O_2+O_2$. It is a powerful oxidising agent. CO is oxidised to $CO_2$ when passed over it at 100°C. The substance is paramagnetic and contains an odd electron in its molecule.

**Potassium Peroxide ($K_2O_2$),** an orange coloured solid, is reported to be formed as the main product by controlled oxidation of potassium in air at 300°C. It reacts with water to give KOH and $H_2O_2$.

**Potassium Hydroxide [Caustic Potash (KOH)]** : It is prepared by the exactly similar methods as those of sodium hydroxide, *viz.* (i) by boiling a solution of potassium carbonate with lime, filtering off the precipitated calcium carbonate and concentrating the filtrate to crystallisation, or (ii) by the electrolysis of potassium chloride solution. The pure product is obtained by the reaction of air-free distilled water on potassium amalgam and evaporating the resultant solution.

Potassium hydroxide is a white crystalline deliquescent solid (m.p. 360°C), highly soluble in water. The solution of KOH absorbs $CO_2$ from air ; but, as potassium carbonate is very soluble in water, the solution does not solidify on such absorption. The water-solution is strongly alkaline and has corrosive action on skin. It is a stronger alkali than NaOH. Strong solutions of KOH slowly attack glass ; the fused solid attacks even platinum. n chemical properties, KOH resembles NaOH very closely.

Potassium hydroxide is used in making **soft** soap. It is also used in the laboratory for absorption of $CO_2$ during its estimation.

**Potassium Chloride (KCl)** occurs in nature as *sylvine* in small quantities. It is generally prepared from *carnallite* in any of the following two ways :

(i) Carnallite is heated little above 161°C. All the magnesium chloride in it melt and remain in the liquid, while almost pure KCl remains undissolved. This is separated and purified by crystallisation from water.

(ii) A hot aqueous solution of carnallite is gradually cooled. Potassium chloride crystallises out first, while the more soluble magnesium chloride remains in solution. The crystals of KCl are filtered and purified by recrystallisation from water. The mother-liquor is used for dissolving fresh batches of carnallite.

Potassium chloride is a white crystalline solid (m p. 790°C), less soluble than NaCl in cold water, but the solubility increases rapidly with the rise of temperature. It resembles NaCl in most of its chemical properties.

Potassium chloride is used in the manufacture of metallic potassium, caustic potash, potassium carbonate, potassium chlorate, potassium dichromate *etc.* It is also used as a fertilizer.

**Potassium Bromide (KBr)** : The mother-liquor left after the preparation of KCl from *carnallite* contains potassium bromide. Bromine obtained from this KBr is allowed to react with iron powder in presence of water, when a solution of iron bromides is obtained. The reaction of the solution of the iron salts with potassium carbonate precipitates hydrated triferric tetroxide, forming KBr in solution. The precipitate is filtered and the filtrate is evaporated to get potassium bromide. $4Br_2+3Fe=FeBr_2+2FeBr_3$ ; $FeBr_2.2FeBr_3+4K_2CO_3+4H_2O=8KBr+Fe_3O_4.4H_2O\downarrow+4CO_2\uparrow$ .

Bromine reacts with a hot and concentrated solution of KOH to form potassium bromide and potassium bromate. The resultant solution is dried and the dry mass is heated with powdered carbon, when potassium bromate is reduced to potassium bromide. The dry mixture is treated with water and filtered. The clear filtrate is concentrated and cooled, when crystals of potassium bromide separate out. They are collected by filtration and dried in air.

$$6KOH+3Br_2=KBrO_3+5KBr+3H_2O\ ;$$
$$KBrO_3+3C=KBr+3CO\uparrow .$$

Potassium bromide is a colourless crystalline solid, highly soluble in water. When $Cl_2$ gas is passed through a solution of potassium bromide, bromine is set free and KCl is formed in solution : $2KBr+Cl_2=2KCl+Br_2$. Hot and conc.$H_2SO_4$ decomposes KBr with the liberation of $Br_2$ and HBr.

$$2KBr+H_2SO_4 = K_2SO_4+2HBr :$$
$$2HBr+H_2SO_4 = Br_2+2H_2O+SO_2$$

It is used in medicine and for the preparation of silver bromide which is used in photography.

**Potassium Iodide, (KI),** is similarly prepared from iodine, as described for KBr. The compound is easily soluble in water and alcohol. Iodine dissolves in an aqueous solution of KI to form a deep brown solution which contains the complex salt, $KI_3$. Potassium iodide is used in chemical analysis and also in medicine.

**Potassium Nitrate ($KNO_3$)** occurs in nature as *nitre* or *saltpetre* in India, Sri Lanka and other tropical countries. $KNO_3$ is formed in the soil by the following process : The oxidation of nitrogenous organic matter by aerial oxygen in the presence of nitrifying bacteria forms nitric acid, which combines with alkali in the soil to produce mainly calcium nitrate and potassium nitrate. Most of the $KNO_3$ is manufactured in India by lixivating soil with water and boiling the solution with wood ashes containing $K_2CO_3$, when calcium nitrate is converted into $KNO_3$ and $CaCO_3$ is precipitated : $K_2CO_3+Ca(NO_3)_2=2KNO_3+CaCO_3$. The precipitated $CaCO_3$ is filtered off and the filtrate is evaporated, mainly in the sun, to obtain crystals of $KNO_3$.

Potassium nitrate can also be obtained on a large scale by the double decomposition of KCl and $NaNO_3$. Saturated solutions of KCl and $NaNO_3$ are mixed together and heated to boiling. The mixture is cooled gradually, when the least soluble salt NaCl crystallises out first and is filtered. The filtrate consists of the hot concentrated solution of $KNO_3$ saturated with sodium chloride. On further cooling, much of the $KNO_3$ crystallises out. The separation depends upon the large difference in the solubility of $KNO_3$ with temperature, while the solubility of NaCl is almost the same in both cold and hot water. The nett effect of this solubility characteristic is that, on cooling, very little NaCl crystallises out with $KNO_3$. The reaction is represented by the equation : $KCl+NaNO_3=KNO_3+NaCl$.

Potassium nitrate is a white crystalline substance, melting at 336°C. It is not deliquescent like $NaNO_3$. It is soluble in water. On heating at high temperatures, $KNO_3$ first fuses and then decomposes to potassium nitrite and $O_2$ : $2KNO_3=2KNO_2+O_2$. Fusing $KNO_3$ is, therefore, a strong oxidising agent so that sulphur, charcoal and phosphorus burn brilliantly in it.

Potassium nitrate is largely used as a fertilizer. It is also used in fireworks composition and in the preparation of gunpowder.

**Potassium Nitrite, ($KNO_2$),** is obtained as a colourless crystalline solid (m.p 441°C), by fusing $KNO_3$ with metallic lead and extracting the cooled melt with water. The addition of alcohol to the water-extract precipitates potassium nitrite : $KNO_3+Pb=KNO_2+PbO$. The compound is highly soluble in water.

**Potassium Sulphate** ($K_2SO_4$) occurs as a constituent of *kainite* (KCl, $MgSO_4$, $3H_2O$ or $K_2SO_4$, $MgSO_4$, $MgCl_2$, $6H_2O$) or *schonite* ($K_2SO_4$, $MgSO_4$, $6H_2O$). It is obtained from kainite as follows :

A hot solution of kainite is cooled, when the double salt, $K_2SO_4$, $MgSO_4$, $6H_2O$ (*schonite*) crystallises out and magnesium chloride remains in solution. It is filtered and the residue dissolved in hot water. To the hot solution, solid KCl is added, when the following reaction takes place :

$$K_2SO_4,\ MgSO_4,\ 6H_2O+2KCl=2K_2SO_4+MgCl_2+6H_2O.$$

On cooling the hot mixture, the least soluble $K_2SO_4$ seperates out as anhydrous crystals. These are collected and dried. $K_2SO_4$ can also be made by heating KCl with conc. $H_2SO_4$ in the proportions represented by the equation, $2KCl+H_2SO_4=K_2SO_4+2HCl$.

Potassium sulphate is a colourless crystalline solid (m.p. 1050°C), moderately soluble in water.

**Uses** : Potassium sulphate is used as a fertilizer. It is also used for manufacturing potash alum and potassium carbonate.

**Potassium Bisulphate** ($KHSO_4$) is prepared by heating $K_2SO_4$ with conc. $H_2SO_4$ and cooling, when the crystals of $KHSO_4$ are obtained : $K_2SO_4+H_2SO_4=2KHSO_4$. It is also formed as a by-product in the preparation of $HNO_3$ from $KNO_3$ and conc. $H_2SO_4$ :

$$KNO_3+H_2SO_4=KHSO_4+HNO_3.$$

Potassium bisulphate forms colourless crystals (m.p. 219°C), soluble in water. The solution is strongly acidic due to dissociation : $KHSO_4\rightleftharpoons K^++HSO_4^-$ ; $HSO_4^-\rightleftharpoons H^++SO_4^{=}$. The salt is transformed to potassium pyrosulphate ($K_2S_2O_7$) on heating to dull redness, but is decomposed to $K_2SO_4$ and $SO_3$ on strong heating :

$$2KHSO_4=K_2S_2O_7+H_2O\ ;\ K_2S_2O_7=K_2SO_4+SO_3.$$

Potassium bisulphate is used as a fertilizer and also in the preparation of potash alum. It is also used in chemical laboratories for cleaning platinum vessels and also as a reagent for decomposing minerals before analysis.

**Potassium Carbonate (Pearl ash, $K_2CO_3$)** was earlier prepared by extracting wood ashes with water, and evaporating the filtered solution to dryness. The residue, on strong heating in iron pots, gave a crude $K_2CO_3$ (called the pot-ash) which was purified by recrystallisation from water.

All plants contain potassium salts (the potassium-content of banana trees is much richer) which are converted to $K_2CO_3$ on burning the dry plants ; $K_2CO_3$ is also obtained by lixivating the burnt residue (molasses) of alcoholic fermentation processes.

Potassium carbonate can not be manufactured by the Solvay process. The high solubility of $KHCO_3$ does not allow its deposition as a solid mass in the carbonating tower. It may, however, be manufactured by the *LeBlanc Process*, as described for $Na_2CO_3$, by using KCl as the starting material, or by the electrolysis of KCl in Hargreaves-Bird-type of diaphragm cell similar to the manufacture of $Na_2CO_3$. It is generally prepared on a large scale by *Precht's Process*. A suspension of hydrated magnesium carbonate in a cold concentrated solution of KCl is treated with a stream of $CO_2$, when the following reaction takes place :

$$3(MgCO_3.3H_2O) + 2KCl + CO_2 = 2(MgCO_3.KHCO_3.4H_2O) + MgCl_2.$$

The double-salt (magnessium potassium hydrogen carbonate) is sparingly soluble in water and as such, it precipitates out. The precipitate is filtered, and the residue heated with water under pressure (in an autoclave) at 140°C, when it undergoes decomposition as follows :

$$2(MgCO_3.KHCO_3.4H_2O) = 2MgCO_3 + K_2CO_3 + 9H_2O + CO_2.$$

The precipitated $MgCO_3$ is filtered off and it can be used again in the process. The solution of $K_2CO_3$ is evaporated and the solid residue in strongly heated to obtain anhydrous $K_2CO_3$.

Potassium carbonate is a deliquescent white solid (m.p. 891°C), soluble in water. It crystallises from aqueous solution as $K_2CO_3.2H_2O$. The aqueous solution reacts alkaine due to hydrolysis : $K_2CO_3 + 2H_2O \rightleftharpoons 2KOH + H_2CO_3$. Potassium carbonate resembles $Na_2CO_3$ in its chemical properties.

Potassium carbonate is used in the manufacture of hard glass and soft soap. Many potassium salts are prepared from it. Anhydrous

$K_2CO_3$ is sometimes used for drying alcohols. It is a constituent of *Fusion-mixture* which is commonly used in inorganic analysis.

[*Fusion-mixture* is a mixture of $K_2CO_3$ and $Na_2CO_3$. It fuses at a lower temperature (712°C) than either of the constituents.]

**Potassium Bicarbonate ($KHCO_3$)** is prepared by passing a stream of $CO_2$ into a saturated solution of $K_2CO_3$ in water. The crystals of $KHCO_3$ slowly separate out. These are collected and dried on a porous plate. $K_2CO_3+H_2O+CO_2 \rightleftharpoons 2KHCO_3$.

Potassium bicarbonate is a white solid, soluble in water. The aqueous solution is strongly alkaline due to hydrolysis : $KHCO_3+H_2O \rightleftharpoons KOH+H_2CO_3$. It decomposes on heating to form $K_2CO_3$, $CO_2$ and $H_2O$ : $2KHCO_3 \xrightarrow{\text{heat}} K_2CO_3+H_2O+CO_2$.

**Potassium cyanide, (KCN)**, is prepared by passing a stream of dry ammonia gas over a mixture of carbon and molten potassium carbonate:

$$K_2CO_3+C+2NH_3=2KCN+3H_2O.$$

After the completion of the reaction, the molten liquid is filtered and cast into solid. It can also be prepared by fusing a mixture of potassium carbonate and potassium ferrocyanide.

$$K_4[Fe(CN)_6]+K_2CO_3=5KCN+KCNO+CO_2+Fe.$$

The molten mass is further reacted with a small amount of charcoal powder to reduce the potassium cyanate (KCNO) formed into KCN.

Potassium cyanide is a hygroscopic, crystalline white solid (m.p. 634.5°C). It is highly soluble in water and is extremely poisonous. An aqueous solution of KCN is alkaline due to hydrolysis :

$$KCN+H_2O \rightleftharpoons \underset{\substack{\text{strong}\\\text{base}}}{KOH}+\underset{\substack{\text{weak}\\\text{acid}}}{HCN}.$$

It is used as a laboratory reagent and also in the extraction of gold and silver and in electroplating.

**Potassium thiocyanate (KCNS)** : This compound is also known as potassium sulphocyanide. It is prepared by melting a mixture of potassium cyanide and powdered sulphur : $KCN+S=KCNS$. The compound is also formed when a mixture of potassium ferrocyanide, potassium carbonate and sulphur powder is heated :

$$K_4[Fe(CN)_6]+K_2CO_3=5KCN+KCNO+CO_2+Fe\ ;$$

$$5KCN+5S=5KCNS.$$

Potassium thiocyanate forms colourless deliquescent crystals which are soluble in water. It is used in the identification of ferric and cobaltous salts.

**Tests for Potassium :** (i) Potassium and its salts produce violet (lilac) colour in the *Flame Test* and the colour appears crimson when seen through double blue glass. (ii) Solutions of potassium salts give yellow precipitates with a solution of sodium cobaltinitrite. (iii) A solution of chloroplatinic acid, when added to a concentrated solution of a potassium salt, gives a yellow precipitate of $K_2PtCl_6$ (Pot. chloroplatinate). (iv) When perchloric acid is added to a fairly conc. solution of a potassium salt, white potassium perchlorate ($KClO_4$) is precipitated. Potassimu is estimated gravimetrically as perchlorate or chloroplatinate. It may also be estimated as anhydrous $K_2SO_4$ like sodium.

## RUBIDIUM AND CESIUM

| | | | |
|---|---|---|---|
| *Symbol* : | Rb | *and* | Cs |
| *Atomic number* : | 37 | *and* | 55 |
| *Atomic weight* : | 85.48 | *and* | 132.91 |

These two heavier alkali metals occur in nature in very small amounts, usually in *Lepidolite* and *Carnallite*, the minerals of lithium and potassium respectively. The mineral *Pollucite* also contains cesium and rubidium. They were discovered by Bunsen and Kirchoff (1860-61) from the spectroscopic examination of the mineral water of Durkheim.

**Extraction :** The alums and chloroplatinates of Rb and Cs are much less soluble than the corresponding compounds of the other alkali metals, and this property is taken advantage of in separating these two metals from the other members of the alkali metals family. The mother-liquor after the extraction of potassium from carnallite, or that after the extraction of lithium from lepidolite, is treated with a solution of ammonium alum and the mixture is evaporated to crystallisation, when the first crop of crystals are obtained as the mixed alums of Rb and Cs. The alums of Rb and Cs may be separated by fractional crystallisation, or by treatment with silico-tungstic acid, when the less soluble cesium salt is precipitated first and separated. The rubidium and cesium compounds separated as above, are converted to chlorides separately, and the metals are obtained by heating the dry chlorides with calcium, barium or iron in vacuum and condensing the vapours of the metals in a glass receiver. Cesium can be obtained directly from the mineral *pollucite* by heating (900°C) the latter with metallic calcium, followed by re-distillation in vacuum at 350°C, or by the reduction of its hydroxide, chloride or carbonate with metals like Mg, Al, Ba, Ca or iron (700—1000°C). The physical properties of the two metals are tabulated below :

| **Property** | **Rubidium** | **Cesium** |
|---|---|---|
| Atomic number | 37 | 55 |
| Atomic weight | 85.48 | 132.91 |
| Electronic configuration | 2.8.18.8.1 | 2.8.18.18.8.1 |
| Colour and state | white, soft | white, soft |
| Melting point (°C) | 38.9 | 28.5 |
| Boiling point (°C) | 700 | 670 |
| Sp. gravity | 1.53 | 1.9 |
| Conduction of heat and electricity | Good conductor | Good conductor |
| Colour of flame | red-violet | red-violet |

Chemically, both the metals are very reactive, Cs is more so than Rb. They readily tarnish on exposure to air and violenty react with water. Rb reacts even with ice at 0°C and Cs with ice at $-116$°C. Cesium is the most electropositive of all the alkali metals. Both of them directly combine with hydrogen, carbon, nitrogen, halogens and sulphur to produce the corresponding binary compounds. The compounds of rubidium and cesium (like oxides, hydroxides, chlorides, carbonates, sulphates *etc.*) are similar to those of the other alkali metals and are analogously prepared.

**Uses** : Rubidium and cesium are used in making photo-electric cells and vacuum tubes.

**Tests** : Rubidium and cesium impart red-violet colour to the Bunsen flame. Both are estimated gravimetrically as sulphate or chloroplatinate.

**FRANCIUM** (Atomic No.$=87$ ; Atomic wt.$=223$), the heaviest member of the alkali metals, was first indentified definitely by Mlle. Percy (1931) in the disintegration products of actinium-227, where it is formed as the minor product (about 1.1%) of $\alpha$-ray decay of the element. It is radioactive ($\beta$-emitter), with a half-life of 21 minutes. Its chemical properties, as much as is known, are similar to the other alkali metals.

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CHAPTER XII

# THE COINAGE METALS

## *The Metals of Group IB*

The three metals—copper, silver and gold—are placed in Group IB of the Periodic Table. Their terrestrial occurrence is not very abundant, but their existence in some concentrated deposits and their desirable properties have made them very familiar, and prompted their production from time immemorial. All these metals are tough, malleable and ductile, possess characteristic metallic lustre and take up a high polish. They are resistant to atmospheric corrosion and do not tarnish in air. These properties made them useful for preparing coins from very ancient times and as such, they are called *coinage* or *currency* metals. They are also used for electroplating and for making jewelleries. Copper, in particular, is used for making utensils, pipelines, many useful alloys and electrical wires and apparatus. All the three metals are good conductors of heat and electricity.

The electronic configurations of the atoms of these three metals, together with their different oxidation states are shown below :

| Metal | Electronic configuration | Oxidation states |
|---|---|---|
| Copper (Cu) | [Ar] $3d^{10}\ 4s^1$ | 1, **2**, 3 |
| Silver (Ag) | [Kr] $4d^{10}\ 5s^1$ | **1**, 2, 3 |
| Gold (Au) | [Xe] $4f^{14}\ 5d^{10}\ 6s^1$ | 1, **3** |

[The numbers in bold type are the principal oxidations state.]

The chief physical properties of the metals are tabulated below :

| Property | Copper | Silver | Gold |
|---|---|---|---|
| Atomic number | 29 | 47 | 79 |
| Atomic weight | 63.57 | 107.88 | 197.2 |
| Electronic configuration | 2.8.18.1 | 2.8.18.18.1 | 2.8.18.32.18.1 |
| Density (20°C), gm/cc. | 8.92 | 10.5 | 19.3 |
| Atomic volume (cc) | 7.12 | 10.27 | 10.22 |
| Melting point (°C) | 1083 | 950.5 | 1063 |
| Boiling point (°C) | 2310 | 1950 | 2600 |
| 1st. ionisation potential, ev. | 7.723 | 7.574 | 9.223 |
| Atomic radius (Å) | 1.173 | 1.339 | 1.336 |
| Ionic radius ($M^+$) (Å) | 0.96 | 1.26 | — |
| Colour of vapour | Green | Blue | Yellowish green |
| Oxidation potential (V) | $Cu \rightarrow Cu^{+2} + 2e$<br>—0.34 | $Ag \rightarrow Ag^{+} + e$<br>—0.7999 | $Au \rightarrow Au^{+3} + 3e$<br>—1.96 |

**Gradation of physical properties :**

(i) **Atomic volume and ionic radius** : Due to the combined effect of the filled penultimate d-orbital and the gradual increase of the nuclear charge, the attraction between the nucleus and the valence-shell of these atoms gradually increases. As a result, the radius and the volume of these atoms become less than those of the atoms of the alkali metals. Among the three coinage metals, the atomic radius and hence, atomic volume increase with the increase of atomic number from Cu to Ag ; but, due to *lanthanide contraction*, the atomic radius and volume of Au are almost equal to those of Ag.

(ii) **Hardness and density** : The increased population of electrons in the penultimate shell results in stronger attraction among the atoms of these elements and this is the cause of the hardness of these metals, which increases gradually from Cu to Au. The increased density of these metals results from the closed packing of their atoms in the solid state in face-centred cubic lattice. The density of these metals gradually increases from Cu to Au

(iii) **Melting and Boiling points** : For the reason stated in (ii) above, the inter-atomic attraction in these metals are quite high and this results in their high melting and boiling points.

(iv) **Ionisation potential, electropositive or metallic character** : Due to the smaller atomic volume and high nuclear charge of the atoms of the coinage metals, the electron in their outermost shell is strongly attracted by the nucleus. So, it is difficult to ionise these atoms by removing the outermost electron. As a result, the coinage metals are not readily oxidised and their ionisation potential or oxidation potential is quite high. [For these reason, the coinage metals act as **noble metals**.] So, the electropositive or metallic character of these metals is quite weak. The order of their electropositive or metallic character decreases in the order, Cu>Ag>Au. So, copper displaces silver and gold from solutions of their salts. This is reflected in the property of their oxides and hydroxides. These metals can be easily separated by electrolysis at different potentials, copper being deposited (at the cathode) at the lowest voltage.

**Gradation of the chemical properties of the coinage metals :**

**(A) Electronic configuration, valency and its nature :**

The electronic configuration, $(n-1)\ d^{10}\ ns^1$, is characteristic of the coinage metals, and many of their properties are natural consequence of such an electronic structure. They are all *transition metals* and, as the energy-difference between the *ns* and (*n*—1)*d* electrons is not large, more than a single electron can be removed from their atoms, and as such, +1, +2 and +3 oxidation-states are generally assumed by these metals. The negative oxidation-states are precluded for these metals. As a cation with 18-electron arrangement in the penultimate shell is capable of deforming an anion more than a cation with 8-electron outer shell (inert gas), covalent compounds of these metals in all the three oxidation-states are common.

(B) **Chemical reactivity :**

The chemical reactivity of the coinage metals is much less pronounced, as already been stated, due to the larger nuclear charge and smaller atomic volume of their atoms, which result in the stronger attachment of the valence-electrons to the atoms and their much less electronegativity. They have greater tendency to form covalent (and co-ordinate covalent) compounds than to form ionic compounds, and the latter, when formed, are generally not very stable. They form monovalent (*-ous*) and polyvalent (*-ic* ; *bi-* or *trivalent*) compounds. In the monovalent compound, the $ns^1$ electron is used and they are generally colourless (unless the anion is coloured), except $Cu_2O$ which is red. The bi- and trivalent compounds are generally deeply coloured. In the formation of these polyvalent compounds, the extra-electrons are drawn out from the (*n*—1)*d* shell. In their simple salts, however, the common valency of Cu is 2, of Ag 1 and of gold 3. The simple salts of monovalent silver are more stable than the monovalent compounds of copper and gold. Thus, for example, $AgNO_3$ and $Ag_2SO_4$ are neither hydrolysed nor decomposed in aqueous solution ; but the simple cuprous and aurous compounds, if not insoluble in water, disproportionate spontaneously in presence of water : $Cu_2SO_4 = Cu + CuSO_4$ ; or, $2Cu^{+1} = Cu^{\circ} + Cu^{+2}$; $3AuCl = 2Au + AuCl_3$; or, $3Au^{+1} = 2Au^{\circ} + Au^{+3}$ Simple copper salts are more stable in the bivalent state of the metal ; the only simple compounds of bivalent silver are its fluoride, $AgF_2$ and perhaps the oxide, AgO (although many complex compounds, containing bivalent silver in the cation and the anion are known) and the bivalent gold compounds are extremely rare, because of the spontaneous disproportionation reaction, $2Au^{+2} = Au^{+1} + Au^{+3}$, leading to the formation of monovalent and trivalent gold compounds. Simple salts of trivalent gold is stable, but similar salts of trivalent copper and silver are unknown. Some compounds of the coinage metals are mentioned below :

(i) **Hydrides :** There is very little evidence for the formation of the hydrides of the coinage metals.

(ii) **Oxides and Hydroxides** : Oxides of these metals in different oxidation states are known, *e.g.* $Cu_2O$ and $CuO$ ; $Ag_2O$ and $AgO$ ; $Au_2O$ and $Au_2O_3$. Of these, $CuO$ and $Ag_2O$ are weakly basic oxides, but $Au_2O_3$ is amphoteric. Except copper, which is transformed into $CuO$ on long heating in air or oxygen, silver and gold do not directly combine with oxygen ; their oxides are prepared indirectly and they decompose into the metal and oxygen on strong heating. The oxides are practically insoluble in water. The hydroxides, $AgOH$, $Cu(OH)_2$ and $Au(OH)_3$ may be prepared indirectly, and they are sparingly soluble in water and are classed as weak bases.

(iii) **Action of acids** : Copper and silver are acted upon by dilute $HNO_3$, but not by dilute $HCl$ or dilute $H_2SO_4$, as they occur below hydrogen in the electrochemical series. (Copper, however, dissolves in dil. $H_2SO_4$ in presence of oxygen, producing $H_2O$ in place of $H_2$.) They dissolve in hot conc. $HNO_3$ and $H_2SO_4$, when oxides of nitrogen and $SO_2$ are formed. Gold is not attacked by any single acid (except selenic acid), but dissolves in aqua-regia to form chloroauric acid, $HAuCl_4$.

(iv) **Chlorides** : All the three metals are attacked by chlorine to give $CuCl_2$, $AgCl$ and $AuCl_3$ respectively. $CuCl_2$ decomposes on heating to $Cu_2Cl_2$ and $Cl_2$ ; $AgCl$ is unaffected by heat and $AuCl_3$ is decomposed into Au and $Cl_2$ on strong heating.

(v) **Cyanides** : The insoluble cyanides of all the three metals are known, and they dissolve in excess potassium cyanide solution to give complex cyanides.

(vi) **Complexes** : The three coinage metals, due to their transitional character, form a host of various complexes in their different oxidation states and they occur either in the complex cations or the complex anions.

Monovalent copper, silver and gold generally forms linear complexes of the type $[ML_2]$ with monodentate ligands ($M=Cu$, Ag or Au and $L=$a monodentate ligand). For example, the following complexes of the metals in the monovalent state are familiar : $[Cu(NH_3)_2]^+$, $[Ag(NH_3)_2]^+$, $[Au(CN)_2]^-$, $[AuCl_2]^-$ *etc.* Divalent copper forms various complexes with monodentate, bidentate and polydentate ligands. Of them, the important examples are : $[Cu(NH_3)_4]^{++}$, $[CuCl_4]^{2-}$, $[Cu(pic)_2]$, $[Cu(acac)_2]$, $[Cu(en)_2]^{++}$ *etc.* [In these examples, pic=anion of picolinic acid ; acac=anion of acetylacetone ; en=ethylene diamine.] The structures of these complexes are either square planar or distorted octahedral. Bivalent silver generally forms square planar complexes such as $[Ag(pic)_2]$. Complexes of bivalent gold are not known. Trivalent gold forms a stable complex with ethylenedibiguanide. Other complexes of $Au^{III}$ are also known. Their structures are generally square planar, or octahedral or trigonal bipyramidal. The following complexes of trivalent gold are worth-mentioning : $[Au(diars)_2I_2]$, $[AuBr_6]^{3-}$, $[Au(o\text{-phen})_3]^{+3}$ (*octahedral*) ; $[Au\ (diars)_2I]^{++}$ (*trigonal bipyramidal*) ; $[Au(diars)_2]^{+3}$, $[AuCl_2Py_2]^+$, $[Au(NO_3)_4]^-$ (*square planar*). [In these examples, *diars*=diarsine ligand ; *o*-phen=ortho phenanthroline ligand ; py=pyridine ligand ]

**Similarities among copper, silver and gold :** The three coinage metals, placed in Group IB of the periodic table, possess striking similarities among themselves. Some of these similarities are mentioned below :

**Electronic configuration of the atoms** : All the three metals possess similar electronic configuration, which is characterised by the structure $[(n-1)d^{10}ns^1]$.

(ii) **Natural occurrence** : Due to their feeble chemical reactivity, these metals sometimes occur the free or native state in nature.

(iii) **Physical properties** : Each of these metals is hard but malleable and ductile. Their melting and the boiling points are very high They are quite dense metals.

(iv) **Chemical reactivity** : With weak electropositive and far less electronegative character, the chemical reactivity of the three metals is very low.

(v) **Variable valency** : As the energy of the $(n-1)d$ and $ns$ electrons does not differ much, the electrons of these two levels of the atoms of the coinage metals can be simultaneously used for the purpose of valency. Thus, all the three metals exhibit variable valency. But, the most normal valency is, Cu=+2, Ag=+1 and Au=+3.

(vi) **Complex formation** : All the three metals form large number of complex compounds.

(vii) **Displacement from solution by other metals** : As these three metals are placed towards the bottom of the electrochemical series of metals, they are displaced from solutions of their salts by metals like Zn, Fe *etc.*

**Position of the coinage metals in the periodic table** : It should be mentioned here that, in the long form of the Periodic Table, the Group IB metals occur in between the Group VIII metals and the Group IIB metals. Thus, Cu lies between Ni (Gr. VIII) and Zn(Gr. IIB), Ag between Pd (Gr. VIII) and Cd (Gr. IIB) and Au between Pt (Gr. VIII) and Hg (Gr. IIB). So, there appear certain similarities between the properties of the coinage metals and those of the platinum metals on the one hand and those of the Group IIB metals on the other hand. Thus, the bivalent cupric salts are similar to the bivalent nickel and zinc salts. The resemblances between Ag and Pd or between Au and Pt are also very striking. They are all noble, shining metals, with high melting points. Their atomic volumes are very small and they are very little reactive, not being attacked by water or air. They invariably form complex salts of similar types as shown below :

| | | |
|---|---|---|
| $K_2[Cu(CN)_4]$ | $K_2[Ni(CN)_4]$ | $K_2[Zn(CN)_4]$ ; |
| $K[Ag(CN)_2]$ | $K_2[Pd(CN)_4]$ | $K_2[Cd(CN)_4]$ ; |
| $[Ag(NH_3)_2]Cl$ | $[Pd(NH_3)_4]Cl_2$ | $[Cd(NH_3)_4]Cl_2$ |

Thus, it appears that the coinage metals form a bridge between the Group VIII metals and the Group IIB metals.

## COPPER

*Symbol* : Cu ; *Atomic No.*$=29$ ; *Atomic wt.*$=63.57$

*Electronic configuration* : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

**OCCURRENCE** : Copper constitute, about $1 \times 10^{-4}\%$ of earths crust. It occurs native to a small extent in nature, but the chief sources are the workable concentrated forms in ores and minerals. The important ores of copper ore : (i) **copper pyrites** or **chalcopyrite** $2CuFeS_2$ (or $Cu_2S$, $Fe_2S_3$), (ii) **chalcocite** or **copper glance**, $Cu_2S$, (iii) **Malachite.** $Cu(OH)_2.CuCO_3$(*green*), (iv) **Azurite**, $2CuCO_3$, $Cu(OH)_2$ (*green*, a rare ore) and (v) **cuprite** or **Ruby ore**, $Cu_2O$ (*red*). In India, the sulphide ore, copper pyrites, is available in small amounts in Bihar (Musabani mines), Rajasthan (Khettry mines), Orissa and Sikkim. Recently, deposits of rich copper ores, estimated to be about three crore tons, have been reported to be occuring in the Alandali area of Karnatak state. Copper is extracted in India at Ghatsila (Bihar) and at Khettry (Rajasthan) factories.

**EXTRACTION** : Despite its low copper-content ($\sim 2\%$), copper pyrites is mainly used all over the world for the extraction of copper. The ore contains considerable amounts of iron sulphide and siliceous matter. The separation of these impurities from copper is made possible by the easier oxidation of the base metal (iron) to ferrous oxide, which readily combines with silica to produce ferrous silicate as slag.

**Concentration of the ore** : At the first step of the metallurgy of copper, the ore is thoroughly washed with water to remove the adhering earthy materials and other impurities. The washed and powdered ore is then concentrated by the froth-floatation process in the following manner : the powdered ore is suspended in water in a tank and a little acid, pine oil and xanthate are added to it. The mixture is then vigorously agitated by blowing air through the bottom of the tank. The metallic ore particles are preferentially wetted by oil and a froth is formed at the surface of the mixture, which contains the sulphide particles. The siliceous impurities are wetted by water, become heavier and settle at the bottom. The froth is skimmed and dried, and then subjected to roasting.

**Roasting** : The concentrated ore contains about 25% of copper. It is roasted in a multiple-hearth furnace in a current of air. The roasted ore comes down from one hearth to another and meets the hot gaseous products passing upwards. Arsenides and sulphides in the ore are oxidised to arsenious oxide and sulphur dioxide respectively and escape as gaseous products. [$SO_2$ produced in this operation may be used for the manufacture of $H_2SO_4$.] Iron and copper sulphides are partially oxidised to FeO and $Cu_2O$. Thus, the roasting leaves the mass as a mixture of oxides and sulphides of the two metals :

$2CuFeS_2 + O_2 = Cu_2S + 2FeS + SO_2$ ;

$2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2$ ; $2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$.

**Smelting** : *First fusion.*—The roasted mass is mixed with siliceous materials (generally, copper ores containing silica, but free from sulphur, is used) and some coke, and strongly heated in a reverberatory furnace (for low-grade ores) or in a water-jacketted blast furnace, having inner lining of firebricks (for high-grade ores). Hot and dry air is passed through holes near the bottom of the furnace, which burns the coke, producing much heat. The sulphides of iron in the roasted ore are oxidised to FeO, but the sulphides of copper are little affected. Silica combines with FeO to form ferrous silicate as slag, which rises up and floats on the heavier molten layer of $Cu_2S$ and FeS. [$FeO + SiO_2 = FeSiO_3$]. The slag is removed and the molten mass is run off and cast into granules. The product is called **coarse metal** or **copper matte**, and it contains about 35% copper and 30% iron

*Second fusion.*—The '**coarse metal**' is subjected to a second roasting, followed by fusion in the above manner, when **fine metal** is obtained.

The product, at this stage, comprises chiefly of $Cu_2S$ (~75-80% copper and 20% sulphur) ; it also contains a very small quantity of iron. The slag formed in the process of the second fusion carries appreciable quantities of copper and, to recover the metal, it is added to the charge of the first fusion.

**Reduction** : Blocks of **fine metal** are heated in a current of air in a reverberatory furnace or a Bessemer converter with siliceous lining Cuprous sulphide is partially converted to cupric oxide during heating, along with the fomation of some cuprous oxide and copper sulphate : $Cu_2S+2O_2=2CuO+SO_2$ ; $2Cu_2S+5O_2=2CuSO_4+2CuO$ ; $2Cu_2S+3O_2=2Cu_2O+2SO_2$. The supply of air is then cut off and the temperature of the furnance is raised. At this stage, **self-reduction** of $Cu_2S$, $CuSO_4$, $Cu_2O$ and $CuO$ takes place to produce metallic copper : $Cu_2S+2CuO=4Cu+SO_2$ ; $2Cu_2O+Cu_2S=6Cu+SO_2$ ; $CuSO_4+Cu_2S=3Cu+2SO_2$. The metal is obtained in the molten state and it is run off from the furnace and cast into moulds. The solid blocks of the metal acquire blistered appearance due to the escape of $SO_2$ through the molten mass during solidification. It is, therefore, called '**blister copper**' and it contains about 98% of copper.

**Refining of Blister Copper** : *Thermal refining.*—Blocks of blister copper are melted in a furnace with a current of air, when the remaining sulphur in it is oxidised to $SO_2$ and escapes ; any residual arsenic is volatilised as $As_2O_3$ ; heavy metals like iron and tin are oxidised to their oxides, which float on the surface of the molten mass because of their lower densities, and are skimmed off. The presence of cuprous oxide in the metal makes it brittle and so, it is reduced to the metallic state by sprinkling powdered anthracite coke over the molten mass and agitating with poles of green wood. Metallic copper obtained by this process is about 99.5% pure and is called **tough pitch** or **marketable copper.**

*Electrolytic refining.*—Copper refined by the thermal methods often contains small quantities of arsenic, bismuth, lead, tin, iron, selenium, tellurium, along with traces of silver and gold. Very pure copper (~99.9% pure) is essential for electrical industries, and the recovery of the precious elements (Ag, Au, Se, Te *etc.*) is also very important. So, the 'tough pitch' is refined electrolytically. Thick blocks of the metal (99.5%) are used as anodes and are placed between thin sheets of pure copper acting as cathodes, in a large electrolytic bath. The bath contains a solution of 15% $CuSO_4$ with 5% $H_2SO_4$ as the electrolyte. On passing electric current, copper dissolves out from the anodes and is deposited on the cathodes. The precious element and the other impurites are obtained as anode slime, which is collected in canvas bags enclosing the anodes. (The precious elements may be recovered subsequently from the anode slime by suitaable processes.)

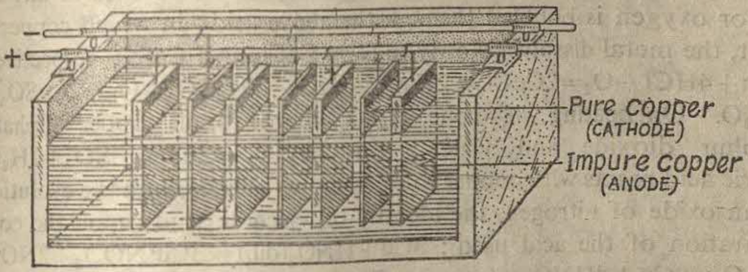


Fig. 12.1—Electrolytic refining of copper.

**Other methods of extraction**: Extraction of copper from very low-grade sulphide ores, containing large quantities of iron sulphide ($Fe_2S_3$), is achieved by the wet process. Huge heaps of such ores are sprinkled with water and allowed to stand exposed to air for a considerable length of time. Aerial oxidation converts the sulphides of iron and copper into ferrous sulphate and copper sulphate respectively, which are leached with water into big tanks. Addition of iron scraps to this solution precipitates copper, which is filtered. It is refined by melting and casting into blocks and subsequent electrolysis.

$$2Cu_2S+5O_2=2CuSO_4+2CuO \;;\; 2Fe_2S_3+11O_2+2H_2O=2H_2SO_4+4FeSO_4;$$
$$CuO+H_2SO_4=CuSO_4+H_2O \;;\; CuSO_4+Fe=FeSO_4+Cu\downarrow.$$

The oxide and carbonate ores may be worked up for the extraction of the metal, either (i) by smelting the powdered ores with coke at high temperatures, when they are reduced to the metallic copper, or (ii) by dissolving the ores in dil. $H_2SO_4$ and electrolysing the resultant copper sulphate solution with copper cathode and lead anode. $Cu_2O+C=2Cu+CO \;;\; CuCO_3+C=Cu+CO+CO_2 \;;$

$$CuCO_3.Cu(OH)_2+2H_2SO_4=2CuSO_4+3H_2O+CO_2.$$

The Hindusthan Copper Corporation, at its Ghatsila and Khettry works, extracts, copper by the **flash smelting process**. This method was developed in Finland in 1949 and it is being put into practice in this country since 1972. The basic idea of this process is to save electric power or fuel during smelting. The heat generated during the oxidation of part of iron and sulphur of the concentrated chalcopyrite ore is utilised for the smelting purpose.

**PROPERTIES : Physical properties** : Pure copper is dull red in colour, with a specific gravity of 8.95 and melting at 1084°C. It is a tough but soft metal which is a good conductor of heat and electricity. It is malleable and ductile.

**Chemical properties** : It is unaffected in dry air, but it gradually becomes coated with a green layer of basic copper sulphate when exposed to moist air. It is oxidised to black CuO only on the surface, when heated in air It is not acted upon by water or alkali. The metal directly unites with halogens and sulphur at elevated temperatures to form the halides and the sulphides respectively. As it occurs below hydrogen in the electrochemical series of metals, it does not liberate hydrogen by dil. or conc. HCl and dil. $H_2SO_4$ in absence of air. If air or oxygen is bubbled through the above acids in which copper is kept, the metal dissolves slowly to form $CuCl_2$ and $CuSO_4$ respectively $2Cu+4HCl+O_2=2CuCl_2+2H_2O$ ; $2Cu+2H_2SO_4+O_2=2CuSO_4+2H_2O$. On heating with conc. $H_2SO_4$, copper forms copper sulphate, sulphur dioxide and water : $Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O$. Nitric acid reacts with copper to form copper nitrate, with the evolution of an oxide of nitrogen, the identity of which depends upon the concentration of the acid used : $3Cu+HNO_3(dil.)=3Cu(NO_3)_2+2NO+4H_2O$ ; $Cu+4HNO_3$ $(conc.)=Cu(NO_3)_2+2NO_2+2H_2O$. In presence of oxygen (or air), copper slowly dissolves in conc. $NH_4OH$ solution to produce deep blue cuprammonium hydroxide : $2Cu+8NH_4OH+O_2=2[Cu(NH_3)_4](OH)_2+6H_2O$. Copper is displaced from solutions of its salts by all metals which are more electropositive than it, and it displaces metals like silver and gold (which are less electropositive than it) from their solutions : $CuSO_4+Fe=FeSO_4+Cu\downarrow$ ; $2AgNO_3+Cu=2Ag\downarrow+Cu(NO_3)_2$.

**Uses** : In electrical industries, copper is extensively used for manufacturing wires (for telegraph, telephone and power lines) and for making plugs, switches and gears (where it serves to establish electrical contact). Copper sheets and plates are used for making boilers, steam pipes, evaporating pans, household utensils *etc.* The metal also finds application in making coins and useful alloys. Copper salts are used in electroplating, electrotyping and in medicines, insecticides, pesticides and paints.

**Alloys of copper** : Copper is an important constituent of many useful alloys. The more important of them are : (i) Brass (Cu, 70; Zn 30), (ii) Bronze (Cu, 92-95; Sn, 8-4; other elements like Si, P *etc.* are often added to make special bronzes); (iii) German silver (Cu, 50; Zn, 30; Ni, 20), (iv) Bell metal (Cu, 80; Sn, 20), (v) Gun metal (Cu, 85; Sn 5; Zn, 10), (vi) Monel metal (Cu, 27; Ni, 68; Fe, 2-5), (vii) Muntz metal (Cu, 60; Zn, 40), (viii) Constantan (Cu, 60; Ni, 40) *etc.*

## COMPOUNDS OF COPPER.

Copper generally forms two types of compounds, *viz.* cuprous and cupric compounds, in which the metal exhibits valency of +1 and+2 respectively

As a member of the transition series of elements and the first coinage metal, copper usually exhibits variable valencies of +1 and +2 units in their compounds. In the cuprous compounds (with +1 oxidation state of the metal), the cuprous ion has $3d^{10}$ electronic configuration, while in the bivalent cupric compounds, the electronic configuration of the metal ion is $3d^9$. The relative stabilities of the two oxidation states are indicated by the following potential values :

$$Cu = Cu^{+} + e,\ E^{\circ} = -0.52V\ ;\ Cu^{+} = Cu^{+2} + e,\ E^{\circ} = -0.153V.$$

$$\text{So, } 2Cu^{+} = Cu^{\circ} + Cu^{+2},\ E^{\circ} = 0.367V\ ;\ K = [Cu^{+2}]/[Cu^{+}]^2 = 1.2 \times 10^6.$$

The potential values show that, although it is easy to oxidise the metal to the +1 state, in aqueous solution the free $Cu^+$ ion can exist only in exceedingly low concentration, and indeed, the only cuprous compounds which are stable to water are the highly insoluble ones like CuCl, CuCN, $Cu_2O$, $Cu_2S$ *etc.*, and the water-soluble cuprous compounds which are strongly complexed by ligands such as $Cl^-$, $CN^-$, $NH_3$, acetonitrile *etc.* Cuprous salts of oxy-anions can be obtained in non-aqueous medium, but salts such as $Cu_2SO_4$ are immediately decomposed by water to give copper and the cupric salt. (This is due to greater lattice- and solvation energies of $Cu^{+2}$ ion than the $Cu^+$ ion.) So, the stability of the cuprous compounds depends much on the nature of the anions or other ligands present, on the dielectric constant of the solution, and in a solid, on the nature of the neighbouring atoms in the crystal.

## CUPROUS COMPOUNDS.

**Cuprous oxide or Red oxide of copper ($Cu_2O$)** occurs in nature as *Ruby copper ore* in small quantities. When metallic copper is heated in air, cuprous oxide is formed along with cupric oxide (CuO) It is best prepared by reducing bivalent copper compounds in alkaline media When alkaline copper tartrate solution (Fehling's solution) is boiled with a solution of glucose, cuprous oxide is formed as a red precipitate. The precipitate is filtered, washed and dried.

Cuprous oxide is a red solid which is soluble in acids, but is insoluble in water and alkali solutions. It dissolves in conc. HCl to form a colourless solution of cuprous chloride, which is gradually oxidised to green cupric chloride by atmospheric oxygen : $Cu_2O + 2HCl = Cu_2Cl_2 + H_2O$. With dil. $H_2SO_4$, it forms copper sulphate in solution, together with the precipitation of metallic copper. On heating with conc $H_2SO_4$, sulphur dioxide, copper sulphate and water are formed : $Cu_2O + H_2SO_4\ (\text{dil.}) = CuSO_4 + H_2O + Cu \downarrow$ ; $Cu_2O + 3H_2SO_4\ (\text{hot, conc.}) = 2CuSO_4 + SO_2 + 3H_2O$. With dil. $HNO_3$, copper nitrate is formed and metallic copper is deposited at the first stage.

The precipitated metal is immediately acted upon by the acid to form copper nitrate, and nitric oxide is evolved : $Cu_2O+2HNO_3=Cu(NO_3)_2+Cu\downarrow+H_2O$ ; $3Cu_2O+14HNO_3=6Cu(NO_3)_2+7H_2O+2NO\uparrow$. The oxide dissolves in ammonium hydroxide to form complex hydroxide : $Cu_2O+4NH_4OH=2[Cu(NH_3)_2]OH+3H_2O$.

**Cuprous Hydroxide, $Cu_2(OH)_2$,** is obtained on treating a solution of cuprous chloride in conc. HCl with an excess of caustic alkali solution. It is an unstable yellow solid, decomposing into $Cu_2O$ and $H_2O$ on slight heating : $Cu_2(OH)_2=Cu_2O+H_2O$. It is insoluble in water, but soluble in acids.

**Cuprous Chloride, $Cu_2Cl_2$ or CuCl,** is prepared either (i) by boiling a mixture of cupric oxide and copper turnings with conc. HCl, until the mixture becomes colourless or white, or (ii) by dissolving $Cu_2O$ in hot, conc. HCl. The clear liquid obtained in either of the above two cases is poured into a large volume of air-free cold water, containing a little dissolved $SO_2$ (to prevent oxidation). White cuprous chloride is precipitated, which is quickly filtered and washed with water, alcohol and ether in succession, and then dried in vacuum : $CuO+Cu+2HCl=Cu_2Cl_2+H_2O$ ; $Cu_2O+2HCl=Cu_2Cl_2+H_2O$.

Cuprous chloride forms white crystals (melting at 422°C) which are insoluble in water. It is fairly stable in dry air, but in moist air, it is slowly oxidised to green basic cupric chloride, $CuCl_2.3Cu(OH)_2.H_2O$. It undergoes hydrolysis, on boiling with water, to precipitate $Cu_2O$ : $Cu_2Cl_2+H_2O=Cu_2O+2HCl$. Conc. HCl dissolves cuprous chloride to form complex compounds like $HCuCl_2$ and $H_2CuCl_3$. It also dissolves in ammonia, and this *ammoniacal cuprous chloride* solution is used to absorb $O_2$, CO and $C_2H_2$. [On absorbing oxygen, the ammoniacal solution of cuprous chloride is converted to cuprammine chloride, $[Cu(NH_3)_4]Cl_2$ ; absorption of CO results in the formation of an unstable carbonyl compound, $CuCl.CO.2H_2O$ ; on absorbing acetylene, cuprous acetylide, $Cu_2C_2$, is precipitated :

$$Cu_2Cl_2+4NH_4OH=2[Cu(NH_3)_2]Cl+4H_2O\ ;$$
$$Cu_2Cl_2+C_2H_2=Cu_2C_2\downarrow+2HCl.]$$

Cuprous chloride is used as an absorbent in gas-analysis and also in purifying gases. It is also used in many organic synthesis.

Cuprous chloride is a covalent compound in the vapour state. Its molecular formula is found to be $Cu_2Cl_2$ from the measurement of its vapour density. The measurement of the depression of freezing point in pyridine, however, indicates that its formula should be CuCl. The close similarity of cuprous chloride and silver chloride (AgCl) suggests that the latter formula is more appropriate for the compound.

**Cuprous Bromide, CuBr or $Cu_2Br_2$,** is formed as pale greenish-yellow crystals (m.p.~500°C) by heating copper powder and bromine vapours at red heat. It is insoluble in water, but is readily soluble in concentrated solutions of ammonia, halogen hydracids and alkali halides to form complex salts as in the case of CuCl.

**Cuprous Iodide, CuI or $Cu_2I_2$,** may be prepared by heating copper with iodine and conc. HI, or by the reduction of $CuSO_4$ solution with alkali iodides. In the latter case, the unstable cupric iodide ($CuI_2$) is initially formed, which immediately breaks up to precipitate cuprous iodide and liberate iodine : $2CuSO_4+4KI=2CuI_2+2K_2SO_4$ ; $2CuI_2=2CuI\downarrow+I_2$. (This preparation is usually carried out in presence of a reducing agent such as $SO_2$ or sodium thiosulphate, when the liberation of iodine is prevented.) The above reaction is used for the estimation of copper iodometrically by titrating the liberated iodine with standard sodium thiosulphate solution in presence of starch solution as indicator.

Cuprous iodide is a white powder, very sparingly soluble in water, but soluble in concentrated solutions of ammonia, halogen acids and alkali halides to form complex salts like those of CuCl and CuBr.

**Cuprous sulphide** ($Cu_2S$) occurs in nature as rhombic crystals of *chalcocite* or *copper glance*. It can be prepared, in almost quantitative yield, as a blackish grey crystalline powder, by heating cupric sulphide (mixed with some sulphur) in a stream of hydrogen. The product melts at 1130°C and has a density of 5.785. It is a fair conductor of electricity. It is practically insoluble in water and ammonium sulphide solution.

**Cuprous sulphate** ($Cu_2SO_4$) is formed as a white powder on heating $Cu_2O$ with dimethyl sulphate at about 160°C : $Cu_2O+(CH_3)_2SO_4=Cu_2SO_4+CH_3.O.CH_3$. The compound readily decomposes into $CuSO_4$ and metallic copper in contact with moisture.

**Cuprous Cyanide, CuCN or $Cu_2(CN)_2$,** is obtained as a white powder (monoclinic prisms) by boiling a cupric salt with potassium cyanide solution till cyanogen gas is completely removed. At the initial stage of the reaction, the unstable cupric cyanide (yellow) is formed, which readily decomposes by heat into insoluble, white cuprous cyanide and cyanogen gas : $2CuSO_4+4KCN=2CuCN\downarrow+2K_2SO_4+(CN)_2\uparrow$.

Cuprous cyanide is insoluble in water and dilute acids, but is soluble in concentrated acids, aqueous ammonia, ammonium salt solutions and especially easily, in alkali cyanide solutions, forming complex salts. $CuCN+3KCN=K_3[Cu(CN)_4]$ (pot. cuprocyanide). Potassium curpocyanide is a very stable complex and has practically negligible dissociation is solution, so that $H_2S$ gas does not precipitate copper from its solution. This forms the basis of separation of copper and cadmium in qualitative analysis, the corresponding cadmicyanide ($K_2[Cd(CN)_4]$) being transformed into CdS by $H_2S$, due to its appreciable dissociation. Solutions of alkali copper (I) cyanides are used in electrodepositing, as baths for copper-plating.

**Cuprous Thiocyanate, CuSCN,** is most readily formed by the addition of potassium thiocyanate or ammonium thiocyanate solution to a solution of cupric salt containing a reducing agent such as $SO_2$ : $2CuSO_4+SO_2+2NH_4SCN+2H_2O=2CuSCN\downarrow+(NH_4)_2SO_4+2H_2SO_4$. It is a white powder, practically insoluble in water and in cold non-oxidising acids, but is soluble in concentrated thiocyanate solution to yield soluble complex salts. Dry cuprous thiocyanate absorbs ammonia in the cold, forming a black powder which easily evolve ammonia again on gentle heating. Due to the sparingly soluble nature of cuprous thiocyanate, copper is often estimated gravimetrically as this salt.

**Cuprous nitrate** and **Cuprous carbonate** cannot be isolated in the pure state.

## CUPRIC COMPOUNDS.

**Cupric Oxide or the Black oxide of copper (CuO)** is best prepared in a pure form by the thermal decomposition of the nitrate, carbonate (or the natural basic carbonates) or the hydroxide of bivalent copper :

$2Cu(NO_3)_2=2CuO+4NO_2+O_2$ ; $CuCO_3=CuO+CO_2$ ; $Cu(OH)_2=CuO+H_2O$. It is a black solid, soluble in acids to form cupric salts, but insoluble in water and alkali solutions. On heating with carbon, hydrogen, carbon monoxide or organic compounds, it readily parts with its oxygen and thus acts as a good oxidising agent : $2CuO+C=2Cu+CO_2$ ; $CuO+H_2=Cu+H_2O$ ; $CuO+CO=Cu+CO_2$. On strong heating above 1100°C, the oxide itself breaks up into $Cu_2O$ and oxygen : $4CuO=2Cu_2O+O_2$.

Cupric oxide is used in the estimation of carbon, hydrogen and nitrogen by combustion methods. It is also used for the manufacture of blue or green coloured glass.

**Cupric Hydroxide, $Cu(OH)_2$,** is formed as a light blue precipitate, on treating a solution of cupric salt with a solution of alkali : $CuCl_2+2NaOH=Cu(OH)_2+2NaCl$.

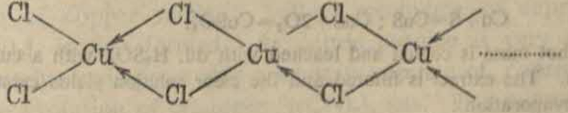
Cupric hydroxide is a pale blue solid, which is almost insoluble in water and alkali solutions, but it dissolves in acids to form the corresponding cupric salts. It also dissolves in ammonium hydroxide solution to form a deep blue solution containing cuprammonium hydroxide : $Cu(OH)_2+4NH_4OH=[Cu(NH_3)_4](OH)_2+4H_2O$. The complex hydroxide is known as **Schweitzer's reagent** and is used in the manufacture of artificial silk. Cupric hydroxide decomposes into black copper oxide on heating, or even on keeping in contact with aqueous solutions for some time : $Cu(OH)_2=CuO+H_2O$.

**Cupric Fluoride ($CuF_2$)** separates from solutions of $Cu(OH)_2$ or $CuCO_3$ in excess of hydrofluoric acid, as light blue, small crystals of composition $CuF_2.2H_2O$. The hydrated salt changes into the white crystalline anhydrous variety (m.p. 950°C) on heating in a current of HF gas. It is sparingly soluble in cold water, but is decomposed by hot water into the basic fluoride, $Cu(OH)F$.

**Cupric Chloride ($CuCl_2$).**—The anhydrous cupric chloride is prepared by heating copper turnings in a current of chlorine gas : $Cu+Cl_2=CuCl_2$. The hydrated salt, $CuCl_2.\ 2H_2O$, may be prepared by the action of HCl on the oxide, hydroxide or the carbonate of the metal. The resultant solution in each case is evaporated to isolate the crystals of the hydrated salt : $CuCO_3+2HCl=CuCl_2+CO_2+H_2O$. On heating in a current of dry HCl gas, the hydrated variety is converted into the brownish-yellow anhydrous salt (m.p. 489°C) which is highly deliquescent. The emerald-green hydrated salt, on gradual heating, first changes to the anhydrous variety and is then decomposed, when red-hot, into cuprous chloride and chlorine : $2CuCl_2=Cu_2Cl_2+Cl_2$. The salt is soluble in water and organic solvents like alcohol, acetone, and pyridine. The aqueous solution is green (or blue when dilute), and it becomes yellow in colour on adding HCl, probably due to the formation of $H_2CuCl_4$ in solution. It is easily reduced to $Cu_2Cl_2$ when its solution in HCl is heated with metallic copper, powdered zinc, stannous chloride or $SO_2$ :

$CuCl_2+Cu=Cu_2Cl_2$ ; $2CuCl_2+Zn=Cu_2Cl_2+ZnCl_2$ ;
$2CuCl_2+SnCl_2=Cu_2Cl_2+SnCl_4$ ;
$2CuCl_2+SO_2+2H_2O=Cu_2Cl_2+2HCl+H_2SO_4$.

X-ray analysis shows that the crystal structure of $CuCl_2$ (and also $CuBr_2$) is of extended chains (as shown below) in which the $Cu^{+2}$ ions are surrounded by Cl-atoms in a square-planar fashion.



**Cupric Bromide, $CuBr_2.2H_2O$,** is obtained as brownish green deliquescent crystals through the action of HBr on $Cu(OH)_2$ or $CuCO_3$. The anhydrous salt forms brilliant, almost black crystals which evolve bromine vapour when heated to red-heat. It resembles $CuCl_2$ in properties.

**Cupric Iodide, $CuI_2$,** is formed initially, on mixing solutions of copper sulphate and potassium iodide ; but, it readily decomposes into white cuprous iodide and iodine. The double salt, $CuI_2.2NH_4I.2NH_3.4H_2O$ is, however, a deep green stable compound.

**Copper nitrate, $Cu(NO_3)_2$,** is formed as a by-product during the preparation of nitric oxide by the action of $HNO_3$ on copper turnings. It is also obtained through the action of $HNO_3$ on CuO, $Cu(OH)_2$ or carbonates of copper : $3Cu+8HNO_3=3Cu(NO_3)_2+2NO\uparrow+4H_2O$ ; $CuO+2HNO_3=Cu(NO_3)_2+H_2O$ ; $CuCO_3+2HNO_3=Cu(NO_3)_2+CO_2+H_2O$. The solid salt [$Cu(NO_3)_2.3H_2O$,] is worked up by evaporating the resultant solutions to crystallisation.

Copper nitrate forms deep blue, deliquescent crystals, $Cu(NO_3)_2.3H_2O$, which are soluble in water and alcohol. The hydrate loses the water of crystallisation on initial heating, but ultimately CuO is formed on strong heating : $2Cu(NO_3)_2=2CuO+4NO_2+O_2$. The salt acts as a strong oxidising agent.

**Cupric sulphide, CuS,** is obtained as a black precipitate when $H_2S$ gas is passed into a solution of a cupric salt, slightly acidified with dil. HCl. It is insoluble in dil. HCl or $H_2SO_4$, but is soluble in hot dil. $HNO_3$. It is slowly oxidised to cupric sulphate, when the moist substance is exposed to air. It breaks up into cuprous sulphide and sulphur on strong heating.

**Copper sulphate, $CuSO_4.5H_2O$, (Blue Vitriol)** : For the demonstration purpose in the laboratory, blue vitriol may be prepared by dissolving CuO, $Cu(OH)_2$ or $CuCO_3$ in dil. $H_2SO_4$ and concentrating the solution to obtain the crystals of the pentahydrate : $CuO+H_2SO_4=CuSO_4+H_2O$ ; $CuCO_3+H_2SO_4=CuSO_4+CO_2+H_2O$. The salt is also obtained as a by-product during the preparation of $SO_2$ from copper turnings and conc. $H_2SO_4$.

*Manufacture of copper sulphate* : (i) *from copper scraps.*—A mixture of copper scraps and sulphur is heated in a furnace, when cupric sulphide is obtained. Heating is then continued in a current of air so that CuS is oxidised to $CuSO_4$ :

$$Cu+S=CuS \; ; \; CuS+2O_2=CuSO_4.$$

The hot mass is cooled and leached with dil. $H_2SO_4$. with a current of air passing on. The extract is filtered and the clear solution yields crystals of blue vitriol on evaporation :

$$CuS+H_2SO_4=CuSO_4+H_2S \; ; \; 2Cu+2H_2SO_4+O_2=2CuSO_4+2H_2O.$$

(ii) *From copper pyrites.*—Copper sulphate is also obtained on a large scale by the *weathering* of copper pyrites ($2CuFeS_2$). The ore is roasted in air under controlled conditions so that copper sulphide is mainly oxidised to $CuSO_4$ and iron sulphide to $Fe_2O_3$. The roasted mass is then extracted with water, when $CuSO_4$ passes into solution along with some ferrous sulphate. The solution is filtered and the filrate is evaporated to obtain crystals of crude copper sulphate. This is recrystallised from water, containing a little $HNO_3$, when ferrous sulphate is oxidised to ferric sulphate and remains in solution due to its greater solubility.

$CuSO_4.5H_2O$ (*blue vitriol*) is a blue crystalline solid. On keeping in air, it effloresces to form the pale blue compound, $CuSO_4.3H_2O$. On heating to about 110°C, these compounds lose water to form the bluish white monohydrate, $CuSO_4.H_2O$. The monohydrate loses the water molecule on heating at 260°C to form the anhydrous salt as a white powder. The anhydrous salt is stable upto 650°C, and above this temperature, it decomposes into CuO, $SO_2$ and oxygen : $2CuSO_4 = 2CuO + 2SO_2 + O_2$. The anhydrous salt readily absorbs moisture and turns blue (due to the re-formation of the pentahydrate). Copper sulphate dissolves in water with slight hydrolysis : $CuSO_4 + 2H_2O \rightleftharpoons Cu(OH)_2 \downarrow + H_2SO_4$. As a result, the aqueous solution of this normal salt reacts acidic and the resultant solution often turns hazy. Addition of alkali solutions to a solution of copper sulphate precipitates copper hydroxide as a blue gelatinous product. Gradual addition of ammonium hydroxide solution to a solution of copper sulphate at first produces a pale blue precipitate of basic copper sulphate, which dissolves on adding excess of $NH_4OH$ solution to form a deep blue solution of cuprammonium sulphate : $2CuSO_4 + 2NH_4OH = (NH_4)_2SO_4 + CuSO_4.Cu(OH)_2$ ; $CuSO_4.Cu(OH)_2 + (NH_4)_2SO_4 + 6NH_4OH = 8H_2O + 2[Cu(NH_3)_4]SO_4$. On adding a solution of potassium iodide to a solution of copper sulphate, a white precipitate of cuprous iodide is formed, together with the liberation of quantitative amount of iodine : $2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 \downarrow + I_2$.

[At the preliminary stage of this reaction, unstable cupric iodide ($CuI_2$) is formed and this is immidiately decomposed into stable cuprous iodide and iodine.

$$2CuSO_4 + 4KI = 2CuI_2 + 2K_2SO_4 \; ;$$
$$2CuI_2 = Cu_2I_2 \downarrow + I_2.]$$

When a solution of potassium cyanide is added to an aqueous solution of copper sulphate, yellow precipitate of cupric cyanide, $[Cu(CN)_2]$, is first formed. As cupric cyanide is very unstable, it immediately decomposes into a white precipitate of cuprous cyanide, with the evolution of cyanogen, $[(CN)_2]$, gas. The cuprous cyanide, thus formed, dissolves in excess of potassium cyanide solution to form a colourless solution of potassium cuprocyanide, $K_3[Cu(CN)_4]$.

$$CuSO_4 + 2KCN = Cu(CN)_2 + K_2SO_4 \; ;$$
$$2Cu(CN)_2 = Cu_2(CN)_2 \downarrow + (CN)_2 \uparrow \; ;$$
$$Cu_2(CN)_2 + 6KCN = 2K_3[Cu(CN)_4].$$

Copper sulphate is used in agriculture as a fungicide and pesticide. It is used in electroplating, electrotyping, dyeing and calico-printing, in medicines, in electric cells, in the preservation of hide and timber. In chemical laboratories, anhydrous copper sulphate is used for detecting and removing traces of water, and as a chemical reagent.

**Copper carbonate ($CuCO_3$)** occurs in nature as the basic salt, *malachite* and *azurite*. The normal carbonate of copper is unknown. A solution of cupric salt reacts with a solution of sodium carbonate to form the basic carbonate of copper : $2CuSO_4+2Na_2CO_3+H_2O=2Na_2SO_4+CO_2+CuCO_3.Cu(OH)_2$. The formation of the basic salt is due to the extensive hydrolysis of $Na_2CO_3$ in solution (forming NaOH), so that $Cu(OH)_2$ is formed along with $CuCO_3$.

The basic carbonates of copper are green to blue solids which are insoluble in water and alkali solutions, but soluble in acids to form the corresponding cupric salts. They decompose to CuO and $CO_2$ when strongly heated : $CuCO_3.\ Cu(OH)_2=2CuO+CO_2+H_2O$.

Basic copper carbonates are used as pigments.

**Cupric acetate, $Cu(CH_3COO)_2.\ 2H_2O$,** crystallises as dark blue-green crystals from solutions of cupric oxide in acetic acid at ordinary temperatures, but the pentahydrate crystallises at low temperatures. The compound is dimeric in nature. It is fairly soluble in alcohol, but is hydrolysed to basic acetate on heating with water.

**Compounds of Trivalent Copper.**

Compounds of copper, in which the metal is present in +3 oxidation state, have been reported from time to time. $Cu^{+3}$ ion has the same electronic configuration as $Ni^{+2}$ ion, and as such, diamagnetic complexes of trivalent copper are quite possible.

Cupric hydroxide dissolves in alkali hypochlortie solutions; the resultant blue solutions are oxidising in nature and evolve oxygen on acidification. These solutions are considered to contain alkali cuprates, $MCuO_2$ (where M=Na or K). Some alkali and alkaline earth metal cuprates has also been prepared as crystalline solids, by heating mixtures of CuO and the corresponding alkali or alkaline earth metal oxides. They are all diamagnetic compounds and have square-planar configuration.

On passing $F_2$ gas through a mixture of solutions of KCl and $CuCl_2$, a pale green crystalline solid, potassium cuprifluoride ($K_3CuF_6$) is obtained. When alkaline solutions of cupric salts, containing potassium periodate or potassium tellurate, are oxidised with alkali hypochlorite or other oxidising agents, compounds such as $K_7\ [Cu(IO_6)_2].7H_2O$ and $K_6H_3[Cu(TeO_6)_2]$ are formed. These are strong oxidising agents and liberate $O_2$ on acidification.

## Complex Compounds of Copper (I) and Copper (II).

As a member of the transition series of metals, copper is well-suitable for forming coordination complexes, both in the monovalent and divalent states. In the cuprous state, the metal ion usually exhibits coordination numbers of 2 or 4, so that the resultant complexes are either linear, square-planar or tetrahedral. In the cupric complexes, the coordination number of the metal ion is usually 4 or 6 and the resultant complexes have square-planar, tetrahedral or distorted octahedral stereochemistry.

**Complexes of monovalent copper :**

Of the cuprous complexes, the following are important : on dissolving insoluble cuprous halides in ammonia, the colourless complexes $[Cu(NH_3)_2]^+$ are formed. Similarly, the halo-complexes, $[CuX_2]^-$, where X is a halogen atom, are formed by dissolving cuprous halides in concentrated halogen hydracid. All these complexes have linear structure. Cuprous cyanide dissolves in alkali cyanide solutions to give cuprocyanide complexes, $[Cu(CN)_2]^-$, which have unusual spiral polymeric structure. On adding excess alkali cyanide solution to CuCN, a soluble complex, $[Cu(CN)_4]^{3-}$ is obtained. This has a tetrahedral stereochemistry. Complex double thiosulphates of monovalent copper, *e.g.* $(NH_4)_2[Cu_2(S_2O_3)_2]$, $Na[Cu(S_2O_3)]$. 1.5 $H_2O$ *etc.* are also known.

**Complexes of bivalent copper :**

A large varieties of cupric complexes are described in literature. A very familiar one is the blue $[Cu(NH_3)_4]^{++}$ complex, formed on adding excess of $NH_4OH$ to a cupric salt solution. Not only ammonia, but other primary amines and diamines (like ethylene diamine) also form well-defined complexes with $Cu^{++}$. Inner-metallic cupric complexes with bidentate mono-acidic ligands (like glycine, picolinic acid, anthranilic acid, salicylaldoxime, acetylacetone *etc.*) are well-known. These complexes are generally insoluble in water, but soluble in organic solvents. *Fehling's solution*, a well-known blue solution formed by the addition of Rochelle's salt (sodium potassium tartrate) to copper soln., is believed to be a polynuclear complex of $Cu^{++}$.

Tests : (i) Copper salts impart a blue-green colour in the *Flame Test*. (ii) On reduction in a charcoal block with sodium carbonate, copper salts form red scales which dissolve in conc. $HNO_3$ to give a blue solution, with the evolution of brown fumes. (iii) *Borax-bead test.*—Copper salts tint the borax-bead *blue* in the oxidising flame and *red* in the reducing flame. (iv) Deposits of metallic copper (red) are formed when a clean iron wire is dipped into a solution of copper salt. (v) A chocolate coloured precipitate (copper ferrocyanide) is obtained when a solution of potassium ferrocyanide is added to a solution of copper salt. (vi) When $H_2S$ gas is passed into a solution of copper salt, acidified with dil. HCl, a black precipitate (CuS) is formed. (vii) When ammonium hydroxide solution is added to a solution of copper salt, at first a pale blue precipitate is formed. This precipitate dissolves on adding more of ammonium hydroxide solution to produce a deep blue solution.

Copper is generally estimated volumetrically by its reaction with KI is weakly acidic medium and titrating the liberated iodine with standard sodium thiosulphate soln. Gravimetrically, it may be estimated as cuprous thiocyanate after precipitating with $NH_4SCN$, or by depositing metallic copper electrolytically.

## SILVER

*Symbol* : Ag ; *Atomic No.*=47 ; *Atomic wt.*=107.88.

*Electronic configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^1$.

**OCCURRENCE** : Small quantities of *native* silver are sometimes found associated with silver ores. The principal ores of the metal are : **Argentite** or **Silver glance** ($Ag_2S$) and **Horn silver** (AgCl), found in large amounts in Bohemia, Colorado, Canada, Chile, Mexico and New South Wales. Other important ores are the *double sulphides* with sulphides of arsenic and antimony. Silver thioantimonite, $Ag_3SbS_3$, occurs as the 'dark-red silver ore', **Pyrargyrite** ; silver thioarsenite, $Ag_3AsS_3$, is found as the 'light-red silver ore', **Proustite**. Silver sulphide also occurs in the form of mixed crystals with *copper glance* ($Cu_2S$), and the mineral is known as **Stromeyerite**, which is, however, poor in the silver-content. The lead ore *galena* (PbS) also contains small quantities of silver sulphide. Silver ores are not available in India, but the metal is obtained in this country as a by-product during copper refining

**Extraction** : Four different processes have been put into practice for the extraction of silver. These are : (i) **Amalgamation process**, (ii) **Wet process**, (iii) **De-silverisation process** and (iv) **Electrolytic process.**

1. The **Amalgamation process** : The process is practically obsolete now-a-days and, as such, a bare outline of the method is mentioned here.

The ore is ground and roasted with sodium chloride to convert the silver compounds into silver chloride (in the case of sulphide ores). The roasted mass is then finely ground with mercury, when metallic silver is produced due to the reaction : $2AgCl+2Hg=2Ag+Hg_2Cl_2$. The liberated silver dissolves in excess of mercury to form an amalgam. The amalgam is distilled to vaporise mercury, when silver is obtained.

2. **Wet process** : (a) **The cyanide process.**—This process has lost its importance at present, partly due to the inherent poison-hazards associated with it and partly due to the recovery of the metal in large

quantities as a by-product in the metallurgy of some less precious metals like copper, lead and zinc.

The finely pulverised ore is agitated in this process with a dilute solution of sodium cyanide. As a result, silver goes into solution as **sodium argentocyanide,** $Na[Ag(CN)_2]$. The reaction involved is represented as follows, taking the sulphide ore as the example : $Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$. The reaction is slow and reversible. So, in order to prevent the reverse reaction (*i.e.* the re-precipitation of $Ag_2S$), about 25-fold excess of NaCN is used. Air is bubbled through the mixture to facilitate the dissolution process by removing the sulphide ions as sulphates through oxidation by aerial oxygen : $Na_2S + 2O_2 = Na_2SO_4$. Aeration also oxidises any metallic silver, present in the ore, into soluble sodium argentocyanide : $4Ag + 8NaCN + O_2 + 2H_2O = 4Na[Ag(CN)_2] + 4NaOH$. After filtration and de-aeration of the solution, zinc or aluminium metal is added to it to precipitate metallic silver : $2Na[Ag(CN)_2] + Zn = Na_2[Zn(CN)_4] + 2Ag \downarrow$. The precipitated silver is separated, washed and purified by melting through *cupellation* or electrolytically.

(b) **The Hypo process** is another *wet process*, in which the finely ground ore, mixed with common salt, is roasted in a furnace, when silver chloride is formed. Silver chloride is then dissolved out by treating the roasted mass with sodium thiosulphate (Hypo) solution : $AgCl + 2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2] + NaCl$. The solution contains silver as the soluble complex salt, sodium argentothiosulphate, which, on treatment with metallic copper, deposits silver in the finely divided state.

In yet another *wet process*, the powdered sulphide ore is roasted, when $Ag_2S$ is converted into $Ag_2SO_4$. Silver sulphate is leached out from the roasted mass with water and the metal is precipitated from the solution by adding copper scraps.

The metal obtained in each of the above two processes is purified as in the *cyanide process*.

3. **The De-silverisation process.**—About two-thirds of the world-production of silver are obtained at present as the by-product from the extraction of copper, lead and zinc.

Silver sulphide is isomorphous with lead sulphide and, as such, it is associated in appreciable quantities with *Galena*, (PbS), the chief ore of lead. The operations involved in the isolation of silver from this lead ore include the enrichment of silver by *Pattinson's* or *Parke's process*. Metallic silver is then obtained by removing lead as PbO by *cupellation*.

(i) *Pattinson's process* : Lead, extracted from galena, often contains upto 5% of silver, and such a sample of lead is called *argentiferous lead.* When molten argentiferous lead is allowed to cool down slowly, almost pure lead solidifies at the freezing point of the metal (327°C). If the solid lead is taken out from the mixture at this point, the liquid alloy left, becomes richer in silver. Solidified lead is removed by perforated ladle, and the enriched mass is cupelled (see below) to recover silver. This process is, however, not in use at present.

(ii) *Parke's process* : This process depends on the fact that the solubility of silver in molten zinc is much greater (300 times) than its solubility in molten lead. Molten lead and molten zinc are almost immiscible, and form separate layers in a mixture ; the upper layer of molten zinc contains 1.2% of lead and the lower layer of molten lead contains 1.6% of zinc. So, on adding zinc to molten argentiferous lead, most of the silver goes into the upper layer (of molten zinc) and forms a silver-zinc alloy. This alloy solidifies on the surface of the molten mass on cooling. It is removed by perforated ladles. [In actual operation, about 1% of Zn is added at a time, the molten mass is stirred well and then cooled to separate the silver-zinc alloy. The operations are repeated till the melt contains only 0.0005% Ag].

The skimmings of the above process contain the Ag-Zn alloy, along with some quantity of lead (due to the small solubility of lead in molten zinc). The zinc is removed from it by distillation from a retort (with a little charcoal to reduce any ZnO formed). The enriched residue contains about 10% Ag and 90% Pb. This is subjected to cupellation to obtain silver.

The amount of silver can also be enriched in an electrolytic process by using the argentiferous lead as anode, when the metal is obtained in the anode slime which collects in canvas bags enclosing the anode.

**Cupellation** : The enriched argentiferous lead is placed in a *cupel* on the hearth of a reverberatory furnace and melted. A blast of air is blown on the molten mass, when lead is oxidised to litharge (PbO), most of which is carried away by the hot air-blast and the remaining portion is absorbed by the porous cupel. The metallic silver is obtained as a bright, molten residue. It is 99.5% pure. Silver of 99.9% purity may be obtained by cupellation at higher temperature.

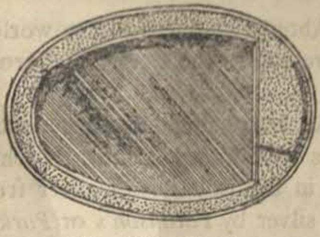


Fig. 12.2—Cupel

A cupel is a somewhat elliptical tray, made of bone-ash, magnesia or portland cement and firebricks. It forms the removable hearth of the furnace, where the charge is heated. It is provided with channels through which molten silver can be drawn off and collected.

4. **Electrolytic Process** : This is generally used to extract the metal from the anode slime formed in the electro-refining of copper. The slime is leached with a mixture of $H_2SO_4$ and $KNO_3$, when copper goes into solution. The residue is dried and fused in a stream of air to oxidise the base metals. The molten silver is separated from the slag of the oxides of the base metals and is finally purified by fusion with nitre. It contains about 96% Ag.

**Refining of Silver** : As extracted by the methods described above, silver almost always contains a little gold, along with some copper. It is refined by *affination* or by electrolytic methods. In the process of *affination*, silver is purified by treatment with hot conc. $H_2SO_4$, when Ag goes in solution (as $Ag_2SO_4$), gold remains as a metallic residue and copper sulphate, which is formed, is mostly precipitated due to its slight solubility in conc. $H_2SO_4$. From the resultant solution, pure silver is precipitated by adding sheets of copper or iron.

Electrolytic refining is more widely employed for the purification of silver. In this process, plates of the metal to be refined (this should contain low percentages of Cu and Pb) are suspended as anodes in a bath of 2.5% silver nitrate solution, containing about 2% free $HNO_3$. Thin sheets of pure silver are used as cathodes. On electrolysis, silver from the anodes go into solution along with lead and copper, and as long as the concentration of the latter metals is not very high as compared with that of silver, only silver is deposited at the cathode. Gold falls to the bottom of the anode, undissolved (and may be collected as spongy mass by putting cloth bags round the anodes). The deposits of Ag on the anodes are brushed off, washed and cast into bars. It has a purity of 99.95% or better.

**Recovery of silver from silver coins** : Silver coins are generally made of alloys of silver and copper. In the process of recovering silver from them, the coins are dissolved in $HNO_3$, when a mixture of silver nitrate and copper nitrate solutions is formed. The mixture is boiled to remove excess of $HNO_3$, and hydrochloric acid is then added to this solution. As a result, silver chloride is precipitated, but copper remains in solution. The precipitated AgCl is filtered, washed with water. Metllaic silver is obtained from this AgCl by any one of the following procedures :

(i) Dry AgCl is fused with excess of anhydrous $Na_2CO_3$, when metallic silver is formed :

$$4AgCl+2Na_2CO_3=4Ag+4NaCl+2CO_2+O_2.$$

(ii) Metallic silver is liberated by reducing AgCl by nascent hydrogen ($Zn+dil.H_2SO_4$) :

$$AgCl+[H]=Ag+HCl.$$

(iii) AgCl is reduced to metallic silver by boiling with NaOH solution and glucose.

Metallic silver, obtained by any one of the above procedures, is refined by fusion with borax and $KNO_3$. It can also be refined electrolytically by using the impure metal as anode and a pure strip of silver as cathode from a bath of $AgNO_3$ solution acidified with nitric acid.

**Properties** : *Physical properties.*—Silver is a tough and shining white, malleable and ductile metal, with a specific gravity of 10.5. It is the best conductor of heat and electricity.

*Chemical properties.*—Silver is unaffected by air, but if air contains $H_2S$, it tarnishes due to the formation of black silver sulphide. Dilute HCl and $H_2SO_4$ have no action on it, but it is attacked by oxidising acids like $HNO_3$ (dil. or conc.) and hot, conc. $H_2SO_4$ : $Ag+2HNO_3=AgNO_3+H_2O+NO_2$ ; $2Ag+2H_2SO_4$ (hot and conc.)$=Ag_2SO_4+2H_2O+SO_2$. [But, when silver is heated to red-heat in HCl gas, it reacts, with the liberation of hydrogen : $2Ag+2HCl=2AgCl+H_2$]. Fused alkali, alkaline solutions or ammonia do not attack silver. It reacts readily with sulphur and halogens on heating to form silver sulphide and silver halides respectively. Because of its position near the bottom of the electrochemical series, any metal (except gold and platinium) displaces silver from solution of its salt : $2AgNO_3+Cu=Cu(NO_3)_2+2Ag\downarrow$. [But, on shaking silver nitrate solution with metallic mercury, silver amalgams of different compositions are formed.]

**Spitting of silver** : When melted in air, silver dissolves about 20 times its own volume of oxygen, which is given off when it is allowed to solidify. This phenomenon of ejection of oxygen by molten silver is called the **spitting of silver.**

**Alloys of silver** : Silver forms alloys with many metals. It is alloyed with copper to render it hard for making jewellery. The parts of Ag per 1000 parts of the alloy is called its *fineness*.

**Uses** : Silver finds many useful applications in everyday life. It is used in making ornaments, silver-wares and coins. It is also used in silver-plating and in preparing mirrors. Colloidal silver is used in medicine and silver salts are used in photography. Many compounds of silver (*e.g.* $AgNO_3$) are prepared from the metal.

## COMPOUNDS OF SILVER.

The predominant oxidation-state of silver in its compounds is the +1 state, although some higher-valent silver oxides, fluorides and complexes are also known.

### Silver (I) Compounds or Argentous Compounds :

**Silver (I) Oxide, $Ag_2O$,** is formed as a brown-black precipitate, on adding alkali solutions to the aqueous solutions of silver salts. It may be assumed that silver hydroxide (AgOH) is first formed, and this immediately passes into silver oxide by loss of water :

$Ag^+ + OH^- = Ag(OH)$ ; $2AgOH = Ag_2O + H_2O$. The precipitate obstinately occludes some of the precipitant (alkalis).

Argentous oxide is sparingly soluble in water. Its suspension imparts a perceptibly alkaline reaction to water, indicating that the second one of the above reactions can be reversed, and the AgOH formed is almost completely ionised to the $Ag^+$ and $OH^-$ ions. It begins to decompose into Ag and $O_2$ on heating even at 190°C and the decomposition is practically complete at 300°C. Decomposition also takes place even at ordinary temperatures on exposure to light. It is reduced by hydrogen even at 100°C. $Ag_2O$ reacts vigorously with hydrogen peroxide at ordinary temperatures and is thereby reduced to metallic silver : $Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$. (This reaction shows the reducing property of $H_2O_2$.) It is a highly basic oxide and absorbs $CO_2$ from air to form silver carbonate. It dissolves in acids to form Ag(I) salts. An aqueous solution of ammonia readily dissolves $Ag_2O$, forming ammine complex : $Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]OH + 3H_2O$. Such a solution, on long standing in air, precipitates a black substance known as *fulminating silver*, which is extraordinarily explosive even in the moist state, as it contains silver nitride, $Ag_3N$. (This substance should not be confused with silver fulminate, AgONC, and silver azide, $AgN_3$.)

**Silver Peroxide** $Ag_2O_2$, is formed as a black powder by the reaction of ozonised oxygen with the finely divided metal, or by treating silver nitrate solution with potassium persulphate : $2AgNO_3 + K_2S_2O_8 + 2H_2O = Ag_2O_2 + K_2SO_4 + H_2SO_4 + 2HNO_3$. (It is not a true peroxide.) Silver peroxide is insoluble in water, but soluble in conc. $HNO_3$. It is a strong oxidising agent and oxidises ammonium salt into nitrate. It decomposes below 100°C. It gives argentous salts and oxygen when heated with acids : $2Ag_2O_2 + 2H_2SO_4 = 2Ag_2SO_4 + 2H_2O + O_2$.

**Silver (I) Sulphide, $Ag_2S$,** is obtained as a black precipitate by the action of hydrogen sulphide gas on any silver (I) salt solution, even in highly acidic medium. It is the least soluble in water of all silver (I) compounds ($K_{SP} \simeq 10^{-50}$). The black coating, often found on silver articles, is $Ag_2S$. It is soluble in alkali cyanide solutions (in presence of air) and also by the action of strong $HNO_3$.

$$Ag_2S+4NaCN \rightleftharpoons 2Na[Ag(CN)_2]+Na_2S\ ;$$
$$Na_2S+2O_2=Na_2SO_4.$$
$$3Ag_2S+8HNO_3=6AgNO_3+4H_2O+3S\downarrow+2NO.$$

It is readily reduced to the metallic state by the action of aluminium in dil. $Na_2CO_3$ solution.

**Silver (I) Sulphate, $Ag_2SO_4$,** forms colourless rhombic crystals (density=5.45 ; m.p.=660°C), and is prepared by the action of conc. $H_2SO_4$ on the metal : $2Ag+2H_2SO_4=Ag_2SO_4+SO_2+2H_2O$, or by adding alkali sulphate or dil. $H_2SO_4$ to a concentrated solution of silver nitrate. It is rather sparingly soluble in water (solubility at 25°C=0.8 gm.), but is more soluble in dil. $H_2SO_4$. The acid sulphate, $AgHSO_4$, crystallizes from the sulphuric acid solution. The acid sulphate is re-converted to the normal sulphate by the action of water. On fusing in an atmosphere of dry HCl gas, silver sulphate decomposes into silver chloride and sulphuric acid : $Ag_2SO_4+2HCl=2AgCl+H_2SO_4$.

**Silver Thiosulphate, $Ag_2S_2O_3$,** is precipitated by adding a solution of sodium thiosulphate to a solution of silver nitrate. It is a white substance, insoluble in water, but soluble in excess of the precipitant, forming complex thiosulphato-argentates of varying compositions. $2AgNO_3+Na_2S_2O_3=Ag_2S_2O_3\downarrow+2NaNO_3$; $Ag_2S_2O_3+3Na_2S_2O_3=2Na_3[Ag(S_2O_3)_2]$. It is decomposed by dilute mineral acids (and also slowly by water), forming black $Ag_2S$ and $H_2SO_4$:

$$Ag_2S_2O_3+H_2O=Ag_2S+H_2SO_4.$$

**Silver (I) Carbonate, $Ag_2CO_3$,** is precipitated as a light yellow substance, when silver nitrate solution is treated with calculated amount of alkali carbonate solution. The use of excess alkali carbonate invariably results in the formation of some $Ag_2O$. It is very little soluble in water, but dissolves in strong alkali carbonate solutions to form soluble complexes such as $K[Ag(CO_3)]$. The dry salt decomposes above 220°C into metallic silver, $CO_2$ and $O_2$ : $2Ag_2CO_3=4Ag+2CO_2\uparrow+O_2\uparrow$. Silver carbonate is decomposed by dilute mineral acid to form the corresponding silver salt, $CO_2$ and water :

$$Ag_2CO_3+2HNO_3=2AgNO_3+CO_2+H_2O.$$

**Silver (I) Cyanide, AgCN,** is precipitated by adding alkali cyanide solutions to the solutions of silver (I) salts. It is a white substance, practically insoluble in water and dilute acids, but readily soluble in alkali cyanide solutions, forming complex salts : $AgCN+KCN=K[Ag(CN)_2]$. The solution of this complex salt is used as electrolyte in silver-plating.

**Silver(I) Thiocyanate, AgSCN,** is formed as a curdy white precipitate on adding potassium thiocyanate solution to a solution of silver nitrate. It is practically insoluble in water and dilute acids, but dissolves readily in excess of the precipitant, forming soluble complexes, thiocyanatoargentates, of which $K[Ag(SCN)_2]$, $K_2[Ag(SCN)_3]$, $K_3[Ag(SCN)_4]$ have been obtained as crystalline mass.

$$AgNO_3+KSCN=AgSCN\downarrow+KNO_3\ ;$$

$$AgSCN+KSCN=K[Ag(SCN)_2]\ ;$$

$$AgSCN+2KSCN=K_2[Ag(SCN)_3]\ \textit{etc.}$$

**Silver (I) Fluoride, AgF,** is obtained as yellow crystals by dissolving $Ag_2O$ or $Ag_2CO_3$ in hydrofluoric acid and concentrating the solution in vacuum. The crystals contain 2 molecules of water of crystallisation. The anhydrous salt is a flaky mass which can absorb large volume of $NH_3$ gas. It is a deliquescent solid and is highly soluble in water. A concentrated solution of AgF dissolves metallic silver, and di-silver fluoride, $Ag_2F$, separates from the solution as bronze coloured hexagonal crystals, having greenish lustre (density=8.6).

**Silver Chloride (AgCl)** is found in nature as *Horn silver*. The compound is generally prepared as a curdy white precipitate by adding a solution of sodium chloride or hydrochloric acid to a solution of silver nitrate in water. The mixture is boiled, and the coagulated precipitate of AgCl is filtered, washed and dried. The compound is also formed on passing chlorine gas over powdered silver at dull-red heat : $AgNO_3+NaCl=AgCl\downarrow+NaNO_3$ ; $2Ag+Cl_2=2AgCl$.

Silver chloride is a white substance, melting at 455°C. It darkens on exposure to light due to some photochemical reduction and, as such, it is used in photography. It is also reduced to the metallic state by heating in a current of hydrogen, or by the action of nascent hydrogen (obtained by the action of dil. HCl on zinc or aluminium powder), or by boiling with glucose in alkaline solution. Fusion with sodium carbonate also reduces AgCl to metallic silver : $4AgCl+2Na_2CO_3=4Ag+4NaCl+2CO_2+O_2$. Silver chloride is insoluble in water and dilute acids. But, it dissolves in conc. HCl and strong NaCl solution, forming $H[AgCl_2]$ and $Na[AgCl_2]$ respectively.

$$AgCl+HCl=H[AgCl_2]\ ;$$

$$AgCl+NaCl=Na[AgCl_2].$$

It is unaffected by conc. $H_2SO_4$ in the cold ; but, on boiling, AgCl is gradually converted into $Ag_2SO_4$ and so it slowly dissolves. It dissolves in ammonia solution to form silver ammine chloride : $AgCl+2NH_3=[Ag(NH_3)_2]Cl$. Solutions of alkali cyanides and alkali thiosulphates also dissolve silver chloride to form soluble complex salts :

$AgCl+2NaCN=NaCl+Na[Ag(CN)_2]$ (Sod. argentocyanide) ;
$AgCl+2Na_2S_2O_3=NaCl+Na_3[Ag(S_2O_3)_2]$ (Sod. argentothiosulphate).

Silver chloride is used in photography.

**Silver Bromide, AgBr,** is obtained as a white to pale greenish yellow precipitate by adding potassium bromide solution to a solution of silver nitrate. The colour of the product depends on the condition of preparation. AgBr also occurs native (as *bromargyrite* ore in Mexico) in admixture with AgCl. It is insoluble in dil. $HNO_3$ and dil. $NH_4OH$ solutions, but is readily soluble in concentrated $NH_4OH$ solution. It is widely used in photography.

In the photographic industry, silver bromide-gelaline emulsions are prepared by mixing gelaline solution, containing KBr, with silver nitrate solution. Silver-bromide is initially formed in a state of extremely fine sub-division. It is then made more photosensitive by prolonged standing in a warm place (*ripening*), so that grain growth occurs.

**Silver Iodide, AgI,** is formed as a yellow precipitate, on adding a soluble iodide solution to silver nitrate solution. It is even more insoluble than AgBr and is not dissolved even by concentrated ammonia solution. It, however, dissolves in an alkali cyanide solution, to form complex salt : $AgI+2KCN=K[Ag(CN)_2]+KI$. It is also appreciably soluble in conc. HI and conc. alkali iodide solutions, especially on warming, to form complex salts such as $K[AgI_2]$, $K_2[AgI_3]$ *etc.* It is used in photography for preparing collodion emulsion plates.

**Silver Nitrate** (*Lunar caustic*, $AgNO_3$) : The salt is generally prepared by dissolving metallic silver in dil. $HNO_3$, and evaporating the solution to crystallisation : $Ag+2HNO_3=AgNO_3+NO_2+H_2O$. It forms colourless crystals (m.p. 217°C), soluble in water. The aqueous solution slowly darkens on exposure to light and, as such, it is generally stored in amber-coloured bottles. When heated to about 500°C, solid $AgNO_3$ decomposes, yielding silver nitrite first and ultimately, metallic silver : $2AgNO_3=2AgNO_2+O_2$ ; $2AgNO_2=2Ag+2NO+O_2$. Dilute HCl or solution of any metallic chloride reacts with an aqueous solution of silver nitrate to give a curdy white precipitate of silver chloride. The precipitate is soluble in ammonia solution, but insoluble in dilute mineral acids. Alkali solutions form a brown precipitate of silver oxide when added to silver nitrate solution : $2AgNO_3+2NaOH=Ag_2O+2NaNO_3+H_2O$. On adding $NH_4OH$ solution to a solution of silver nitrate, the brown precipitate of $Ag_2O$ is first formed, but the precipitate dissolves in excess of $NH_4OH$

solution to give a colourless solution which contains the complex compound, $[Ag(NH_3)_2]OH$ :

$$2AgNO_3+2NH_4OH=Ag_2O+2NH_4NO_3+H_2O\ ;$$
$$Ag_2O+4NH_4OH=2[Ag(NH_3)_2]OH+3H_2O.$$

Similar are the reactions of silver nitrate with solutions of the alkali metal thiosulphates and cyanides. For example, when a solution of sodium thiosulphate or sodium cyanide is added to a solution of silver nitrate, at first a white precipitate of silver thiosulphate or silver cyanide is formed. The resultant precipitate dissolves on adding excess of the precipitant to form colourless, soluble complexes, *viz.* sodium argentothiosulphate or sodium argentocyanide respectively :

$$2AgNO_3+Na_2S_2O_3=Ag_2S_2O_3\downarrow+2NaNO_3\ ;$$
$$Ag_2S_2O_3+3Na_2S_2O_3=2Na_3[Ag(S_2O_3)_2].$$
$$AgNO_3+NaCN=AgCN\downarrow+NaNO_3;$$
$$AgCN+NaCN=Na[Ag(CN)_2].$$

Silver nitrate is reduced to finely divided metallic silver in contact with organic tissues. Skin is, therefore, stained black in contact with this salt. It is also reduced to the metal in contact with paper, cotton, cork, glucose, tartaric acid *etc.*

Silver nitrate is used for making silver halides for photography, for electroplating and making silver mirrors. Silver nitrate is widely used as a reagent in chemical analysis, and to a lesser extent as a caustic in surgery.

**Argentous Complexes :** A great variety of silver (I) complexes are known in solution and in the solid state. The most stable Ag(I) complexes have the linear structure, L—Ag—L (where L is a monodentate ligand) ; the chelating ligands generally tend to form polynuclear complex ions. $[Ag(OH)_2]^-$ is known in strongly alkaline media. $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[AgI_2]^-$ ions are commonly formed, as discussed in the chemistry of $Ag^+$ salts. The existence of soluble complex carbonate, $K[AgCO_3]$, thiosulphates and thiocyanates have also been discussed above.

### The use of silver halides in Photography.

The photographic plates or films, as are commonly used, consist of thin glass plates or strips of cellulose acetate, coated with a layer of colloidal gelatinised silver halides (mainly silver bromide). For making transparent slides *etc.*, AgCl-gelatine plates, or plates with AgCl and AgBr are used. Under the influence of light, photochemical decomposition of the silver halide takes place in traces, where it is illuminated, forming extremely fine particles of metallic silver, whose number is roughly proportional to the quantity of light falling on the film or the plate, provided the exposure is short. Thus, a *latent image* of the object is produced which, of course, makes little visible change on the film or plate. Such latent images are then developed by treatment with suitable reducing agents (called *developers*) such as hydroquinone, metol *etc.*, when more of the silver halide in the previously illuminated portions are reduced to metallic silver. As a result, coating on the plates or films become much darkened at these points. This operation is known as **'development'** of the plate or the film. The next operation, which is known as **'fixing'**, consists of putting the *developed* plate or film in a fixing bath containing a solution of sodium thiosulphate (*hypo*), when the unaltered silver halides on the plate or film is dissolved out : $AgBr+2Na_2S_2O_3=Na_3[Ag(S_2O_3)_2]+NaBr$. [In fact, solution of any other compound which converts silver halides to soluble complexes, *e.g.* KCN, may also be used.] The *picture* that emerges on the plate or the film at this stage is the *negative*, in which the blackenings correspond to the brightest parts of the original object (*i.e.* those parts which received the most light). From this *negative*, the *positive*, with proper distribution of light and dark, is obtained by the process known as **printing.** In this process, the negative is laid on a *print paper* coated with light-sensitive emulsion and the assembly is exposed to light. In so doing, the blackened areas on the *negative* protect the underlying emulsion from light, whereas the portions not blackened allow the light to pass through. The distribution of light and dark is thus once more reversed. The plate or film is then washed with sodium thiosulphate solution, rinsed with water and dried. Thus, we get the photograph of the original object.

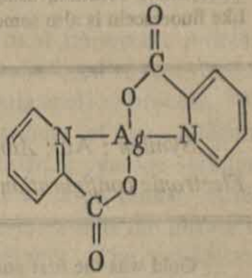
### Compounds of Bivalent Silver : Argentic Compounds.

Although $Ag^{++}$ is iso-electronic with $Cu^{++}$, only two well-defined binary compounds of bivalent silver are known, *viz.* the oxide, AgO and the fluoride, $AgF_2$. Solutions of $Ag^{++}$ in perchloric and nitric acids may, however, be prepared by the oxidation of $Ag^+$ with ozone. The catalytic effect of $Ag^+$ in various oxidations by persulphate (*e.g.*, the oxidation of $Mn^{++}$ to $MnO_4^-$) is believed to be due to the transient formation of $Ag^{++}$ and/or $AgO^+$ ions which are strong oxidising agents.

**Silver (II) Oxide, AgO,** is best prepared as a black precipitate by the oxidation of $Ag_2O$ in a basic medium at about 90°C with potassium persulphate. It is stable to about 100°C and dissolves in acids, evolving $O_2$ and giving $Ag^+$ salts, along with a little $Ag^{++}$ salts in solution. It is a powerful oxidising agent and oxidises iodine to periodic acid. Modern researches point out that it is probably a mixed oxide of monovalent and trivalent silver, $Ag^{+1}Ag^{+3}O_2$.

**Silver (II) Fluoride, $AgF_2$,** is obtained as a dark brown crystalline solid, when AgF is heated with $F_2$ or other fluorinating agents. It is an authentic $Ag^{++}$ compound, and acts both as a strong oxidising agent and a fluorinating agent.

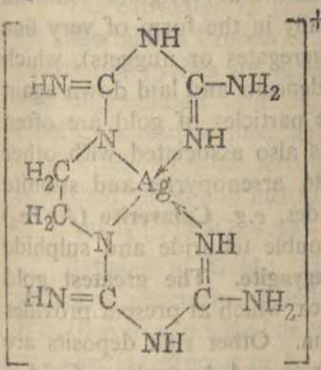
Quite a large number of $Ag^{++}$ complexes are known. The cationic complexes $[Ag(py)_4]^{++}$, $[Ag(dipy)_2]^{++}$, $[Ag(o\text{-phen})_2]^{++}$, (where py=pyridine, dipy=dipyridyl and *o*-phen=ortho-phenanthroline), are obtained as crystalline persulphate salts, on mixing aqueous solutions of persulphate and $AgNO_3$, containing excess of the ligands. From these salts, the other salts of non-reducing anions (*e.g.* $NO_3^-$, $ClO_3^-$, $ClO_4^-$ *etc.*) may be prepared metathetically. The picolinate complex of $Ag^{++}$ is obtained as a very stable, red crystalline compound by the electrolytic or persulphate oxidation of $Ag^+$ salts in presence of picolinic acid.



Silver (II) picolinate

**Tripositive Silver Compounds.**

Simple compounds of trivalent silver are rare and the reported isolations are often controversial. A peroxide, $Ag_3O_4$, has been reported (1921) to be formed by the persulphate oxidation of $AgNO_3$. Anodic oxidation of $Ag^+$ salts in alkaline solution gives a black oxide, which has been claimed to be impure $Ag_2O_3$. Some complex $Ag^{III}$ salts are, however, definitely known. The complex fluorides, $KAgF_4$ and $CsAgF_4$, have been obtained (1953) as yellow compounds, on heating 1:1 mixtures of potassium or cesium fluoride with silver halides in a stream of fluorine. Some tellurato- and periodato-complexes of the type $Na_6H_3[Ag(TeO_6)_2]$ and $K_6H[Ag(IO_6)_2]$ have been isolated (1941). All these complexes contain $Ag^{III}$ in the anions. The most remarkable and stable cationic $Ag^{III}$ complexes have been described by Ray and co-workers (1944 and later) in the form of ethylenedibiguanide complexes. The sulphate salt of this complex is obtained as a red compound, when $Ag_2SO_4$ is oxidised with aqueous potassium persulphate solution in presence of ethylenedibiguanide sulphate. The hydroxide, nitrate and perchlorate of this complex have been prepared metathetically. Besides ethylenedibiguanide, some mono-biguanides also give similar $Ag^{III}$ complexes.



$Ag^{III}$ ethylenedibiguanide complex

**Tests :** Qualitatively, silver is detected by the formation of white curdy precipitate of AgCl, which is insoluble in $HNO_3$, but soluble in $NH_4OH$. Gravimetrically, silver is estimated by weighing as AgCl after drying at 110°C, or by electrolytic deposition and weighing as metal. Volumetrically, silver is titrated with standard NaCl solution, using $K_2CrO_4$ indicator, or with standard ammonium thiocyanate solution, using ferric alum soln. as indicator. Adsorption indicator like fluorescein is also sometimes used.

## GOLD

*Symbol* : Au ; *Atomic No.*=79 ; *Atomic weight*=197.2

*Electronic configuration* : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^1$

Gold was the first pure metal known to man. It has been much valued since the very earliest times. It occupies a very unique and special position because of its almost worldwide status as a monetary standard, against which national currencies are compared. The earliest mine working, of which traces remain, was on gold, and gold washing is depicted in monuments dating back to 2900 B.C.

**OCCURRENCE** : Due to its noble character, gold is generally found free in nature, either as *reef* gold or *alluvial* gold. Gold which is found still in its primary ore deposits is known as *reef* gold. *Alluvial* gold is also invariably found native, usually in the form of very fine grains (and also occasionally as large aggregates or nuggets), which have been removed from its original ore deposits and laid down again is secondary deposits. The fine metallic particles of gold are often dispersed through quartz (sand) and it is also associated with other sulphide ores such as pyrite, chalcopyrite, arsenopyrite and stibnite *etc.* The important ores are the tellurides, *e.g.* **Calaverite** ($AuTe_2$) and **Sylvanite** ($AgAuTe_4$), as also the double telluride and sulphide of lead, gold and antimony, called **Nagyagite.** The greatest gold producing area of the world is South Africa, which at present provides about two-thirds of the world production. Other rich deposits are available in U.S.A., Canada, Russia, Mexico and Australia. Gold is mined in the Kolar gold-field (Karnatak) in India and its annual raising amounts to about 2% of the world production.

**Extraction** : **(1) Sedimentation process** : Gold is extracted from crushed alluvial deposits or auriferous sand through the sedimentation or washing process, by agitating with water in cradles, whereby the specifically heavier grains of gold settle out faster and enrichment is thus attained. This oldest process has been technically improved in *hydraulic mining*, in which powerful jets of water are employed. The process is made technically economic by coupling with the **amalgamation process.** Here mercury is added to the enriched mass, when it dissolves gold to form an amalgam, from which gold is recovered by distilling off mercury. [This method is generally applicable if the particles of gold are not too small, as they are not sufficiently wetted by mercury.] Kolar fields in India use this process.

(2) **The Cyanide Process** : This is the most important process now-a-days for the extraction of gold. This is also used to recover the last portion of gold (*tailings*) left out in the amalgamation process. In this process, the finely divided ore (or the *tailings* of the amalgam process) is agitated or leached with 0.3% potassium cyanide solution (made alkaline with lime) in a current of air in large tanks. After settling, the mixture is filtered through a filter-press and the filtrate is reduced by adding metallic zinc (or aluminium). The precipitate formed is washed, dried and then fused with lead, and the alloy containing about 10% gold is cupelled. The following reactions take place in the cyanide process in the presence of aerial oxygen :

$$2Au+4KCN+2H_2O+O_2=2K[Au(CN)_2]+2KOH+H_2O_2\ ;$$
$$2Au+4KCN+H_2O_2=2K[Au(CN)_2]+2KOH\ ;$$
$$2K[Au(CN)_2]+Zn=K_2[Zn(CN)_4]+2Au\downarrow .$$

The extraction of gold from auriferrous pyrites is effected by the (3) **Chlorination Process** of Percy and Plattner (1846). In this process, the roasted pyrites are moistened with water in tubs with false bottoms, and impregnated with $Cl_2$ gas for about 24 hours. Auric chloride ($AuCl_3$) is thus formed, and this is extracted with water and the gold is precipitated with ferrous sulphate or charcoal. The precipitate is washed, dried and melted as in the cyanide process.

$$AuCl_3+3FeSO_4=Au\downarrow+FeCl_3+Fe_2(SO_4)_3.$$

**Refining of Gold** : Gold extracted by any one of the above processes generally contains copper, silver, zinc *etc.* as impurities. It is, therefore, purified or refined to get pure gold, either by the *Parting* or *Liquation Process* or by the *electrolytic process.* In the parting or liquation process, the impure gold is boiled with conc. $H_2SO_4$, when practically all the impurities go into solution and gold is left behind as a brown powder which contains a little silver. The powder is, therefore, washed with $HNO_3$ and then with water. The dried mass is finally fused with borax and nitre, when pure gold is obtained. Parting can also be done with 60% $HNO_3$.

[The above treatment with conc. $H_2SO_4$, which is often called **quartation**, is not very effective when more than 33% of Au is present in the impure metal, as at that condition, silver is not dissolved. If it contains more gold, it is melted with silver until it contains about one-quarter its weight of gold, and hence this operation is termed quartation.]

The *electrolytic refining* is more widely used. In this process, the gold blocks to be refined are suspended as the anodes in a solution of chloroauric acid ($HAuCl_4$) and pure gold strips are used as cathodes. On starting electrolysis, pure gold is dissolved from the anodes and is deposited on the cathodes. Silver is deposited as AgCl (the anodes are frequently cleaned to remove deposits of AgCl on them) and lead is deposited as $PbSO_4$ by adding $H_2SO_4$. Platnium metals fall to the bottom unacted.

**Properties :** Gold is the *king of metals*, which has a beautiful yellow colour, lustre and is quite stable in air. It is soft, malleable and ductile (density=19.3, m.p.=1063°C and b.p.=2610°C). The electrical and thermal conductivities of gold are very high. It forms alloys with many metals like platinum, palladium, silver, copper *etc*. As a decidedly noble metal, it is practically unchanged in air or in contact with water. It is also very resistant to other forms of chemical attack. Dry gaseous halogens have little action on gold at ordinary temperatures, but the metal is readily attacked by aqueous solutions of chlorine or bromine at ordinary temperatures to form $AuCl_3$ and $AuBr_3$ respectively. Single mineral acids have no action on gold (but it dissolves in selenic acid), but it dissolves readily in aqua regia, and this action is due to the production of nascent chlorine. $Au+3NO_3^-+4Cl^-+6H^+ =AuCl_4^-+3NO_2\uparrow+3H_2O$. (Gold, however, dissolves in conc. $H_2SO_4$ in presence of oxidising agents such as iodic acid, nitric acid, $MnO_2$ *etc*.) The insolubility of the metal in the less strongly oxidising acids is a consequence of its position in the electrochemical series. Gold is not attacked by caustic alkalis, even when fused ; but, it readily dissolves in alkali cyanide solution in presence of aerial oxygen (as stated in the cyanide process of its extraction). Solutions of gold salts (*e.g.* chloride) are reduced by many reducing ions such as $Sn^{++}$, $Fe^{++}$, $SO_3^=$, $NO_2^-$ *etc*, as also by hydrazine and many organic compounds such as formaldehyde, oxalic acid, tartaric acid, reducing sugars, carbon monoxide, acetylene *etc*. In all these cases, the reduction is effected to the metallic state, mainly in the colloidal form (*hydrosols*) which are usually intensely coloured [purple (of Cassius),* blue, violet, brown, black *etc*.]. When alloyed with other metals, the term **carat** is used to express the amount of gold present,—24 carats being pure gold. The parts by weight of pure gold that are present in 24 parts of the gold-alloy is the measure in *carats* of the said alloy. 18-carat gold contains 75% (by weight) pure gold and 25% other metals (such as copper). In American dollar, which is 21.6-carat gold, there is 90% pure gold and 10% copper.

**Uses :** Gold is used as a valued metal for making jewellery and coins. (As pure gold is soft, it is usually alloyed with copper or silver for these purposes.) Considerable quantities of gold are used for electroplating (gilding). It is also used as a solder for platinum and also in medicine. Colloidal gold is used in making **gold ruby glass.**

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*__Purple of Cassius :__ In 1865, Cassius found that, when a solution of gold chloride is reduced by stannous chloride, a purple coloured colloidal solution of gold is formed. This gold-sol is, therefore, known as the purple of Cassius.

$$2AuCl_3+3SnCl_2=2Au+3SnCl_4.$$

The stannic chloride, formed in the reaction, is immediately hydrolysed in solution to form a colloidal solution of meta stannic acid. This colloid adsorbs the reduced gold particles to produce the purple coloured colloidal solution.

## COMPOUNDS OF GOLD.

Gold generally forms two series of salts—*aurous* and *auric* —in which the metal is in the oxidation-states of +1 and +3 respectively. Of the two series of compounds, the auric compounds are more stable ; but, all gold compounds easily decompose with the separation of the metal, either by gentle heat or by the action of reducing agents. No simple gold cations ($Au^+$ or $Au^{3+}$) exist in aqueous solutions. $Au^+$, like the cuprous ion, exists only in very small concentrations in solutions, and hence there are no soluble simple gold (I) salts. Even the very insoluble AuCl is decomposed by water to give metallic gold and hydrolysed gold (III) species. Bivalent stable gold compounds are not known.

### Aurous Compounds.

**Aurous Oxide, $Au_2O$,** has been reported to be formed as a violet-grey powder by heating aurous hydroxide to about 200°C, but the compound has not been well-characterised.

**Aurous Hydroxide, Au(OH),** is obtained as a dark violet precipitate on treating aurous chloride with cold dilute alkali solutions.

**Aurous Chloride, AuCl,** is formed as a pale yellow powder by the thermal decomposition of auric chloride ($AuCl_3$) at 185°C : $AuCl_3 = AuCl + Cl_2$. When more strongly heated, AuCl decomposes into gold and free chlorine. It is readily decomposed by water at ordinary temperatures : $3AuCl = AuCl_3 + 2Au \downarrow$. It dissolves in alkali chloride solutions, forming complex chloroaurate(I) ions, $[AuCl_2]^-$ : $AuCl + KCl = K[AuCl_2]$. But, these also soon decompose in solution, forming complex ions of gold (III) and precipitating metallic gold.

**Aurous Bromide, AuBr,** is prepared from $AuBr_3$ by a method similar to that of AuCl. It resembles AuCl in its properties.

**Aurous Iodide, AuI,** is obtained as a lemon yellow powder, on dissolving auric oxide in hydroiodic acid, or by adding potassium iodide to gold (III) salt solutions. It is also formed by the direct union of gold and iodine at about 110°C. It resembles AuCl and AuBr in its properties, but is more readily decomposed by heat, and less readily hydrolysed by water than the other two halides.

**Aurous Sulphide, $Au_2S$,** is prepared by saturating potassium aurocyanide $K[Au(CN)_2]$ solution with $H_2S$ and then adding hydrochloric acid. The precipitate of $Au_2S$ is steel grey when moist, but brown-black when dry. It is practically insoluble in water and dilute acids, but is decomposed and dissolved by strong oxidising agents like $Cl_2$.

or aqua regia. It dissolves in alkali cyanide solutions to form complex cyanoaurate (I) salts and is also soluble in excess of alkali sulphide solutions to form different thioaurate (I) salts.

**Aurous Cyanide, AuCN,** is obtained as yellow microscopic hexagonal plates, by warming potassium cyanoaurate (I), $K[Au(CN_2]$, with HCl at 50°C : $K[Au(CN)_2]+HCl=AuCN\downarrow+KCl+HCN$. It is sparingly soluble in water and dil. acids, but is readily soluble in alkali cyanide solutions, forming complex cyanoaurate (I) or aurocyanide salts : $AuCN+KCN=K[Au(CN)_2]$. It is also soluble in sodium thiosulphate, ammonium sulphide, caustic potash and $NH_4OH$ solutions, forming complex salts.

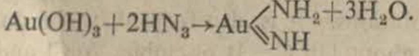
The structure of the complex aurocyanide or cyano-aurate (I) ion is linear, as shown below :

$$\left[:N\equiv C-Au-C\equiv N:\right]^-$$

**Auric Compounds.**

**Auric Oxide ($Au_2O_3$ and Auric Hydroxide [$Au(OH)_3$] :** When a solution of auric chloride is treated with alkali solutions, or is boiled with $Na_2CO_3$ solution, a yellow brown precipitate of auric hydroxide, contaminated with the precipitant, is formed. This is dehydrated over phosphorus pentoxide to give an orange powder of composition AuO(OH), which on careful heating (140—150°C) forms auric oxide as a brown-black powder. Auric oxide is an amphoteric oxide and dissolves both in concentrated acids to form auric salts, and in hot alkali solutions to give aurate (III) salts, *e.g.* $K[AuO_2].3H_2O$. It begins to lose oxygen from about 160°C and is ultimately converted into metallic gold through the intermediate formation of aurous oxide.

Auric hydroxide (whose preparation has been stated above) is also amphoteric in nature. It forms an olive-green explosive powder, called *fulminating gold*, on treatment with ammonia :



$$Au(OH)_3+2HN_3\rightarrow Au\begin{cases}NH_2\\NH\end{cases}+3H_2O.$$

Fulminating gold

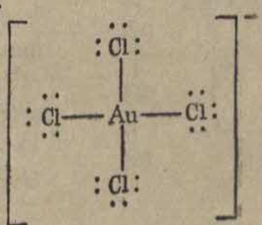
**Auric Chloride, ($AuCl_3$)** and **Auric Bromide ($AuBr_3$)** are obtained, by direct interaction of the elements at about 200°C, in the vapour state, which can be condensed in a cooled receiver as red crystalline needles. Both the compounds are dimeric in nature. They are soluble in water, in which they are partially hydrolysed. On addition of excess halogen hydracids, complex species $HAuCl_4$ and $HAuBr_4$

(chloroauric and bromoauric acid respectively) are formed. The anhydrous halides, as well as the acids, are soluble in organic donor solvents.

[**Chloroauric acid** can also be prepared by dissolving gold in aqua regia and evaporating several times with HCl. It crystallises in long, bright yellow needles of the tetrahydrate, $HAuCl_4.4H_2O$, which effloresce in moist air. It is soluble in water, alcohol and ether, and can be obtained in the anhydrous state by crystallising from alcohol.] Auric chloride deomposes to aurous chloride on heating at 175°C ; on stronger heating, metallic gold is formed,

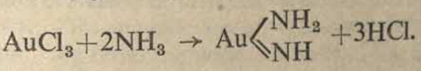
$$AuCl_3 = AuCl + Cl_2 \; ; \; 2AuCl = 2Au + Cl_2.$$

The structure of $AuCl_4^-$ ion is square-planar, as shown in the margin. On adding excess of potassium cyanide to a solution of auric chloride and on cooling the mixture, colourless plates of potassium auricyanide, $K[Au(CN)_4].1.5H_2O$, are formed : $AuCl_3 + 4KCN = K[Au(CN)_4] + 3KCl$. The hydrated salt may be made anhydrous by carefully heating at 200°C. As the metal ion is strongly complexed in this compound, it cannot be reduced to the metallic state by reducing agents like $FeSO_4$.



The structure of $[Au(CN)_4]^-$ ion is also square-planar like the $AuCl_4^-$ ion.

When ammonia is added to a solution of auric chloride, olive-green fulminating gold is precipitated :



$$AuCl_3 + 2NH_3 \rightarrow Au\begin{matrix} \diagup NH_2 \\ \diagdown\!\!\diagdown NH \end{matrix} + 3HCl.$$

**Complex Salts of Gold.**—The chemistry of gold is essentially a chemistry of its complex compounds. It has already been mentioned that several stable aurous complexes such as $[AuCl_2]^-$, $[Au(CN)_2]^-$ and the thiosulphato complex, $[Au(S_2O_3)]^{3-}$, are formed in aqueous solution.

The corresponding salts of these complex ions have also been isolated in many cases. All these complexes are generally monomeric [unlike cuprous and Ag(I) complexes which are polymeric]. The trialkyl-phosphine complex of Au (I), *viz.* $R_3P.AuCl$, has also been isolated. Many complexes of gold (III) are also known. Of these, the tetrahaloaurates (III) and tetracyanoaurate (III) have already been mentioned. A deep red dipyridinodibromo auric bromide,

$[Aupy_2Br_2]Br$, has been obtained by treatment of auric bromide with pyridine. Using chelating ligands, bis-ethylenediamine gold (III) bromide, $[Au(en)_2]Br_3$, and a varieties of diarsine complexes have been isolated.

**Tests :** (i) Gold is generally detected by means of reducing agents which deposit fine brown powder of metallic gold from its salts. If $SnCl_2$ soln. is used as reducing agent, a dilute solution of gold salts produces intense purple colour (*purple of Cassius*) of colloidal gold. For quantitative determination, gold is usually deposited from its solution in the metallic state by reducing agents, and is weighed in that form after washing and strong heating.

## CHAPTER XIII

# ELEMENTS OF GROUP II

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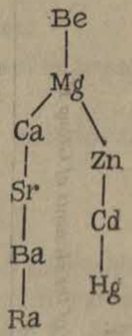
The Group II of the Periodic Table contains nine elements, all of which are metals, *viz.* beryllium, magnesium, calcium, strontium, barium, radium, zinc, cadmium and mercury. As in the preceding Group I, these nine metals are divided to belong to two sub-groups, A and B, the first six metals being included in Group IIA and the latter three (Zn, Cd, Hg) in Group II B. Beryllium and magnesium, appearing in the first and the second short periods of the Periodic Table respectively, are reckoned as the *representative* or *typical elements* of Group II, and they constitute the main sub-group along with Ca, Sr, Ba and Ra. The metals Mg, Ca, Sr and Ba are often called the *alkaline earth* metals due to the alkaline nature and resistance to heat of their oxides. Radium, the heaviest metal of the sub-group A, is radioactive.



The two typical elements, Be and Mg, resemble sometimes the elements of the sub-group A and sometimes those of the sub-group B. Thus, magnesium forms the bicarbonate, $Mg(HCO_3)_2$ similar to $Ca(HCO_3)_2$, but Zn, Cd and Hg do not form bicarbonates. On the other hand, magnesium sulphate and zinc sulphate are isomorphous and similarly hydrated ($MgSO_4.7H_2O$ and $ZnSO_4.7H_2O$). The sulphates of Be and Mg are soluble in water like the corresponding salts of Zn, Cd and Hg ; but, the sulphates of alkaline earth metals, especially, $BaSO_4$ and $SrSO_4$, are sparingly soluble in water. Zinc and cadmium have the same crystal structure as beryllium and magnesium. Mg forms a hydride like those of Ca, Ba and Sr, but the metals Zn, Cd or Hg do not form any hydride. Be and Mg have certain amount of complex-forming capability like the three transition metals of sub-group B, *viz.* Zn, Cd and Hg, which are good complex-formers, but the elements of sub-group A are devoid of this property. Mg (and to some extent, Ba) forms organo-metallic compounds, as do the metals of the sub-group B, but the metals of sub-group A do not form such compounds. The oxides of Mg and of the sub-group A metals are mainly basic due to the more electropositive character of these metals (BeO is, however, amphoteric), but the oxides of the sub-group B metals are not basic due to their less pronounced electropositive nature. The salts of Be and Mg share the property of those of the sub-group B metals of not giving any flame colouration, but the salts of all the metals of sub-group A give characteristic flame colouration.

Apart from the resemblances of the two typical elements, Be and Mg, with the members of the two sub-groups, Be resembles closely Al, the second element of Group III, and Mg resembles Li, the first member of Group I (diagonal relationship) in many properties.

TABLE 13.1.

*Some Important physical properties of the elements of Group II*

| Property | Be | Mg | Ca | Sr | Ba | Ra* | Zn | Cd | Hg |
|---|---|---|---|---|---|---|---|---|---|
| Atomic number | 4 | 12 | 20 | 38 | 56 | 88 | 30 | 48 | 80 |
| Atomic weight | 9·02 | 24·32 | 40·08 | 87·63 | 137·36 | 226·05 | 65·38 | 112·4 | 200·6 |
| Outer electronic configuration | $1s^2 2s^2$ | $2s^2 2p^6 3s^2$ | $3s^2 3p^6 4s^2$ | $4s^2 4p^6 5s^2$ | $5s^2 5p^6 6s^2$ | $6s^2 6p^6 7s^2$ | $3d^{10} 4s^2$ | $4d^{10} 5s^2$ | $5d^{10} 6s^2$ |
| Density (gm./c.c.) | 1·86 | 1·75 | 1·55 | 2·6 | 3·59 | (5·0) | 7·14 | 8·64 | 13·546 |
| Atomic volume (c.c.) | 4·85 | 14·00 | 26·08 | 34·01 | 38·26 | (45·21) | 9·17 | 13·01 | 14·82 |
| Atomic radius (Å) | 0·889 | 1·364 | 1·736 | 1·914 | 1·981 | — | 1·249 | 1·413 | 1·440 |
| Ionic ($M^{+2}$) radius (Å) | 0·31 | 0·65 | 0·99 | 1·13 | 1·35 | — | 0·74 | 0·97 | 1·10 |
| 2nd Ionisation potential (ev) | 18·206 | 15·03 | 11·87 | 10·98 | 9·95 | (10·10) | 17·89 | 16·84 | 18·65 |
| Melting point (°C)** | 1280 | 651 | 851 | 800 | 850 | (960) | 419·4 | 320·9 | —38·9 |
| Boiling point (°C)** | 1500 | 1107 | 1487 | 1366 | 1537 | (1140) | 907 | 767·3 | 356·95 |

*Radioactive, **Divergent values are reported in different studies.

**Differences of beryllium and magnesium from the other alkaline earth metals :**

Although beryllium and magnesium have been placed in Group IIA together with the alkaline earth metals, they differ substantially in certain respects from the latter. The important differences are :

(i) Be and Mg are not readily attacked by dry air and do not decompose water at ordinary temperatures.

(ii) Be dissolves in alkali solutions with the formation of beryllates of the alkali metals.

(iii) The sulphates of Be and Mg are soluble in water.

(iv) The carbonates of Be and Mg are not precipitated by ammonium carbonate in the presence of ammonium chloride.

(v) The salts of Be and Mg do not impart any characteristic colour to the flame.

**General Characteristics of Group II elements.**

The elements of Group II of the Periodic Table are all silver-white metals. The members of the two sub-groups, A and B, of this group are much more alike than those of the preceding Group I. Some important physical properties of these metals are given in Table 13.1. Calcium, strontium, barium and radium are readily oxidised on exposure to air (the metals with higher atomic weights are oxidised more easily than those with lower atomic weights); but, mangesium and zinc are oxidised only slowly at ordinary temperatures, and beryllium, cadmium and mercury are little affected when exposed to air at ordinary temperatures. The electro-affinity of the metals decreases in the order (Ra)$<$Ba$<$Sr$<$Ca$<$Mg$<$Be$<$Zn$<$Cd$<$Hg, that is, from the heaviest element of the sub-group A to the heaviest element of the sub-group B, the typical elements having the intermediate position. The action of water on the metals ranges from Ba to Hg in the manner expected from the trend of their electronegativities. Thus, Ba reacts very vigorously with water and Hg does not react with water under any condition. Of the intermediate metals, Ca and Sr decompose cold water, powdered Mg decomposes hot water and heated Zn and Cd decompose steam.

The usual valency exhibited by all the elements of this group is 2. (This is also probably true for the mercurous compounds, $Hg_2X_2$). This is expected for the electronic configuration of the valence-shells, *viz.* $ns^2$ and $(n-1)d^{10}ns^2$ of the atoms of the Group II A and Group IIB elements respectively. In the case of the elements of sub-group A, the complete octet of the penultimate quantum shell effectively screens the electrons in the periphery (the outermost valence-electrons) from the attractive influence of the positive nucleus. So, the two valence electrons are easily removed, resulting in the formation of a bivalent cation. Indeed, the second electron is removed more easily than the first, so that the two are lost together, leaving no opportunity for these elements to behave as monovalent ones. The electronic configuration of the resultant divalent cation is that of the inert gas preceding the metal. So, the removal of further electrons from this stable inert gas-configuration is not possible from these cations by ordinary chemical processes. The metals, therefore, never display valencies higher than 2. Thus, the metals of Group II A generally form electrovalent compounds in the $+2$ oxidation state of the metals.

[It may be mentioned that sub-halides like $Ca_2Cl_2$ and $Be_2Cl_2$, and sub-oxides like $Ca_2O$ and $Ba_2O$ have been reported in literature.]

Beryllium, with its small size and high ionisation potentials, have some special features. The bonding in its compounds with the most electronegative elements, such as BeO and $BeF_2$, have partial covalent character ; simple $Be^{++}$ ions are rare. $BeCl_2$ is practically covalent and polymeric. The metal forms complex ions and organometallic compounds. Its oxides and hydroxides are amphoteric in character.

For the elements of Group IIB also, the 2 electrons of the outermost quantum shell ($ns$) are used together for valency purposes, so that these elements are also uniformly bivalent. But, the small atomic volumes of these three elements, coupled by the weak screening effect of the $(n-1)d^{10}$ electron-shell, results in the stronger attraction of the peripherial electrons by the nucleus. This makes the removal of the 2 electrons in the $ns$ shell somewhat difficult and, consequently, these elements tend to form covalent compounds and complex ions.

The alkaline earth metals (Ca, Sr, Ba) of the sub-group A form salt-like hydrides, $MH_2$, (a property resembling that of the alkali metals), but the other elements of the group do not form hydrides. Magnesium and the elements of sub-group A form nitrides of the formula $M_3N_2$ on heating in nitrogen, but the other elements of the group do not directly combine with nitrogen to form nitrides, but they may be prepared indirectly. Carbides of Mg, Ca, Sr and Ba are known, but the other metals do not form carbides.

All the elements of this group form basic oxides (ZnO is amphoteric). The colour of the oxides of Be, Mg and metals of sub-group A are white ; ZnO is white in the cold, but it becomes yellow when hot, CdO is brown, $Hg_2O$ is black and HgO is yellow to red. All the oxides are refractory, except those of mercury, which decompose into $O_2$ and the metal on heating. BaO forms $BaO_2$ when heated in air, SrO also forms $SrO_2$ when heated with oxygen under pressure ; the other metals of this group do not form peroxides under such conditions, although they sometimes form unstable hydrated peroxides by indirect means. Except mercury, all the metals of Group II form alkaline hydroxides of the formula $M(OH)_2$, the hydroxides of Be and Zn are, however, amphoteric. The hydroxides of Be, Mg and of the sub-group B metals are sparingly soluble in water, but those of Ca, Sr and Ba are more or less soluble—the solubility increasing with the increase of the atomic weight of the metal.

The sulphides of Be, Mg and of the sub-group A metals are not precipitated by $H_2S$ from solutions of their salts, as they are easily hydrolysed by water ; but, the sulphides of Zn, Cd and Hg are insoluble in water. ZnS and CdS are soluble in HCl, but HgS dissolves only on boiling in aqua regia.

The fluoride of Mg and of the sub-group A metals are sparingly soluble in water but the fluorides of the rest of the elements of this group are soluble in this solvent. The chlorides, bromides and iodides of these metals are also more or less soluble in water (mercurous chloride is soluble in aqua regia only). All the halides of this group of metals (except Ba) are soluble in alcohol. $BeCl_2$ and $HgCl_2$ are soluble in ether also.

All the metals of this group, except mercury form normal carbonates, $MCO_3$, which are more or less insoluble in water and are decomposed by strong heat into $CO_2$ and the corresponding metal oxides. Calcium and magnesium form soluble bicarbonates, stable only in solution. Beryllium, magnesium and the metals of sub-group B form basic carbonates also.

The nitrates of all the metals of this group are known and they are all soluble in water.

Sulphates of all the metals are known. Beryllium, magnesium and the metals of sub-group B form water-soluble sulphates, but those of Ca, Sr, Ba and Ra are sparingly soluble in water—the solubility decreasing with the increase of atomic weight of the metal.

The metals of sub-group B, *viz.* Zn, Cd and Hg, occur at the end of the three *transition series* respectively, and as such, they are capable of forming complex ions. Of the other metals of this group, only Be and Mg show this property to certain extent. The metals of sub-group B and Be and Mg also form organo-metallic compounds. The other metals do not form such compounds.

**Speciality of Mercury :**

The chemistry of mercury, the last metal of the B sub-group, is something special. It is a liquid metal. It is the only metal of this group which gives two series of compounds, *viz. mercurous* and *mercuric* compounds, with entirely different reactions. Coming after gold at the end of the third transition series, mercury exhibits certain nobilities like the former. It is a silver-white liquid metal and, with unusually high ionisation potential and very negative electrode potential, it is chemically somewhat inert and resembles the *noble metals.* It does not form a stable hydroxide or carbonate, and its oxide (HgO) is decomposed on strong heating into oxygen and the metal. These properties of mercury are due to the *inert pair effect* in the electronic structure of the mercury atom. The mercurous salts closely resemble those of silver and monovalent copper ; the mercuric compounds are similar to those of bivalent copper, zinc and cadmium. Mercuric chloride is mainly covalent. Although the mercurous compounds seem to contain univalent mercury, physical studies of mercurous salts indicate the existence of $Hg_2^{++}$ or -Hg-Hg- complex ions. So, it appears that the metal in the mercurous compounds is only univalent in the electrochemical sense, but it is formally bivalent. (For detailed proofs, the section on **mercurous compounds** may be seen.)

## ELEMENTS OF SUB-GROUP A

## BERYLLIUM

*Symbol* : Be ; *Atomic No.*=4 ; *Atomic wt.*=9·02 ;
*Electronic configuration* : $1s^2 2s^2$

**OCCURRENCE** : Beryllium was first detected in 1798 by the French chemist, Vaquelin in the mineral *beryl*, and he called the metal *glucinum* (due to the sweet taste of its oxide). The metal was isolated by Wohler and Bussy in 1828. The metal is fairly distributed in nature, although in small quantities. The principal ore is *beryl*, $Be_3Al_2(Si_6O_{18})$ or $3BeO.Al_2O_3.6SiO_2$. It contains 11—15% of BeO. Other ores are *chrysoberyl*, $BeO.Al_2O_3$ or $Al_2(BeO_4)$ and *phenacite*, $2BeO.SiO_2$ or $Be_2(SiO_4)$. Certain beryl ores are frequently found in very beautifully coloured pieces and are used as gems under the names *emerald* and *aquamarine*. Beryl is available in the mica-mining districts of Bihar (Hazaribag area), in Rajasthan (Ajmer-Marwara area) and in Tamilnadu (Nellore area).

**EXTRACTION** : Beryllium is usually extracted from beryl, by first converting it to BeO and subsequently reducing BeO with carbon.

**Isolation of BeO** : Of the various methods of obtaining BeO from beryl, the silicofluoride method is widely used at present. In this method, the powdered ore is fused at high temperatures with twice its weight of sodium silico-fluoride and a little NaF, when sodium fluoberyllate and cryolite are formed : $3BeO.Al_2O_3.6SiO_2+6Na_2SiF_6=3Na_2BeF_4+2Na_3AlF_6+3SiF_4+9SiO_2$. The liberated $SiF_4$ reacts with NaF to form $Na_2SiF_6$ which is used again : $2NaF+SiF_4=Na_2SiF_6$. The powdered ore may also be heated with a mixture of $Na_2SiF_6$ and $Na_2CO_3$ to minimise the loss of $SiF_4$ : $3BeO.\ Al_2O_3.\ 6SiO_2+2Na_2SiF_6+Na_2CO_3=3Na_2BeF_4+8SiO_2+Al_2O_3+CO_2$. The cooled melt is repeatedly leached with hot water, when $Na_2BeF_4$ goes into solution. The filtered extract is treated with alkali hydroxide or lime-water to precipitate $Be(OH)_2$.

$Be(OH)_2$ is ignited to BeO which is purified by heating in a current of carbonyl chloride at 450°C, when iron and aluminium volatilise as chlorides, calcium is converted to water-soluble $CaCl_2$, but BeO remains unaffected. The residue is leached with water, when $CaCl_2$ dissolves and pure BeO remains insoluble,

**Reduction of BeO** : Finely powdered BeO is mixd with coke and heated in an A.C. electric arc furnace. The furnace is a big graphite crucible, lined with steel sheets, the upper cylindrical portion of the furnace being also made of steel. The crucible part of the furnace is enclosed in fire-brick casing (Fig. 13.1) A tap-hole is provided at the bottom of the crucible for removal of the molten metal. The graphite crucible acts as one electrode and the other electrode is an assembly of adjustable graphite rods, suspended from the top of the furnace. The charge of BeO and coke is fed through a feeder at the top of the furnace. On operating the furnace, BeO is reduced to the metal and melted at the prevailing high temperature, and CO escapes through an opening at the top. The molten metal is tapped through the tapping hole.

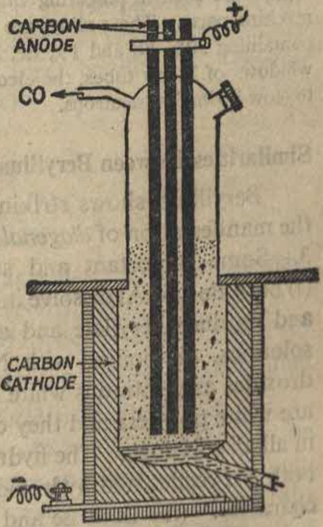


Fig. 13.1

Pure beryllium may be prepared by distilling the metal, obtained in the above process, under reduced pressure, when 99.5% pure Be distils over. The solid metal is collected on cooling the vapours.

**Electrolytic method** : Pure beryllium metal may also be obtained by electrolysing a fused mixture of beryllium chloride and sodium chloride (with a small amount of $CaCl_2$) at 800°C in a wrought iron crucible (cathode), using graphite anode. A fused mixture of beryllium chloride, sodium chloride and beryllium fluoride may also be used as the electrolyte.

**Properties** : Beryllium is a hard, silver-white metal with sp. gr. 1.88. It melts at 1280°C and boils at 1500°C. The metal is transparent to X-rays. It burns with a dazzling flame in air and forms BeO. It is without any action on cold water, but boiling water slowly converts it to $Be(OH)_2$. It directly combines with halogens, sulphur, nitrogen, phosphorus, carbon and silicon to form the corresponding binary compounds. Dil. HCl and dil. $H_2SO_4$ readily dissolve beryllium, but cold and conc. $HNO_3$ makes it *passive*. $Be+2HCl=BeCl_2+H_2$. (It also liberates hydrogen from dil. $HNO_3$.) But, on heating with conc. $H_2SO_4$, it forms beryllium sulphate and sulphur dioxide : $Be+2H_2SO_4=BeSO_4+SO_2+2H_2O$. On boiling with conc. $HNO_3$, beryllium forms beryllium nitrate, with the evolution of nitrogen dioxide : $Be+4HNO_3=Be(NO_3)_2+2NO_2+2H_2O$. It also dissolves in strong alkalis to form beryllates : $Be+2NaOH=Na_2BeO_2+H_2$.

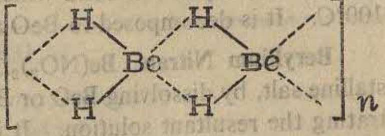
**Uses** : Beryllium is largely used for making very hard alloys. An alloy of Cu with Be (containing about 2.5% Be) is about as hard as steel. Alloys containing Be are used in preparing vital aeroplane parts, ammunitions and other strong machine parts. These alloys are generally non-sparking and non-magnetic. Steel, containing 30% Ni and 1% Be, is rust-proof. Beryllium is also used for making windows of X-ray tubes, the electrodes of neon-lights and also in atomic reactors to slow down fast neutrons.

## Similarities between Beryllium and Aluminium.

Beryllium shows striking resemblance with aluminium, which is the manifestation of *diagonal relationship* as already discussed in chapter 3. Some important and striking points of the resemblance are : (i) both Be and Al dissolve in strong alkali solution to liberate hydrogen and produce beryllate and aluminate respectively in solution. These solutions, on boiling with $NH_4Cl$, precipitate the corresponding hydroxides as gelatinous white substances. (ii) The oxides of Be and Al are white powders and they dissolve in acids (unless ignited) as well as in alkali solutions. The hydroxides have also similar reactions. Thus, both the oxides and hydroxides of these two metals are amphoteric in character. (iii) Both Be and Al form covalent, volatile chlorides. In the anhydrous state, they fume in air. (iv) The salts of both these metals are hydrolysed by water, giving acidic reaction in solution. (v) Both Be and Al can be obtained by the electrolysis of their compounds. (vi) The two metals are often associated with each other in nature.

COMPOUNDS OF BERYLLIUM.

**Beryllium Hydride,** ($BeH_2$), is not formed by the direct union of the two elements, but is formed by the action of $LiAlH_4$ on dimethyl beryllium, $(CH_3)_2Be$, or by the thermal decomposition of $[(CH_3)_3C]_2Be$ (di-*t*-butyl beryllium). It is a white solid, which decomposes to $Be(OH)_2$ and $H_2$ by the action of water. $BeH_2 + 2H_2O = Be(OH)_2 + 2H_2$. It also breaks up into the elements on heating above 125°C. The general properties of $BeH_2$ suggest that it is polymeric with hydrogen bridging, as shown above.



**Beryllium Oxide** (BeO) is a white crystalline substance and is obtained by burning the metal in air (or oxygen), or by the thermal decomposition of its hydroxide, carbonate, nitrate or sulphate. It is very hard and refractory, insoluble in water, but soluble in both acids and alkalis due to its amphoteric nature. It is generally used in glass industry and in the preparation of gas-mantle and hard crucibles.

**Beryllium Hydroxide,** $Be(OH)_2$, is formed as a gelatinous white precipitate, when a solution of beryllium salt is treated with $NH_4OH$. It is amphoteric in nature, and dissolves in acids, as well as in solutions of alkalis and ammonium carbonate to form beryllates. Aqueous solutions of beryllates decompose into $Be(OH)_2$ again on boiling.

$Be(OH)_2 + 2HCl = BeCl_2 + 2H_2O$ ;
$Be(OH)_2 + 2NaOH = Na_2BeO_2 + 2H_2O$ ;
$Be(OH)_2 + Na_2CO_3 = Na_2BeO_2 + CO_2 + H_2O$ ;
$Na_2BeO_2 + 2H_2O = Be(OH)_2 \downarrow + 2NaOH$.

**Beryllium Fluoride** ($BeF_2$) is obtained as a glassy hygroscopic mass by heating solid ammonium fluoberyllate, $(NH_4)_2BeF_4$ :
$BeO + 2NH_4HF_2 = (NH_4)_2BeF_4 + H_2O$ ; $(NH_4)_2BeF_4 = 2NH_4F + BeF_2$.

It is soluble in water and the solution decomposes to beryllium oxyfluoride on heating : $BeF_2 + H_2O = Be(OH)F + HF$.

**Beryllium Chloride,** $BeCl_2 . 4H_2O$, is obtained by dissolving the metal, or its oxide, hydroxide or carbonate in dilute HCl and concentrating the resultant solutions. The anhydrous salt is generally prepared by heating the metal or a mixture of BeO and carbon in a stream of dry chlorine : $BeO + C + Cl_2 = BeCl_2 + CO$. It is a white solid, soluble in water. The anhydrous salt is fusible and volatile, and it fumes in moist air. It is also soluble in organic solvents like chloroform, benzene etc.

**Beryllium Carbonate,** $BeCO_3.4H_2O$, is prepared by adding ammonium carbonate solution to a solution of beryllium salt, and then passing $CO_2$ through the resultant suspension of the basic carbonate. It is a white crystalline solid which becomes anhydrous on heating at 100°C. It is decomposed to BeO and $CO_2$ on stronger heating.

**Beryllium Nitrate,** $Be(NO_3)_2.3H_2O$, is obtained as a white crystalline salt, by dissolving BeO or $Be(OH)_2$ in conc. $HNO_3$ and concentrating the resultant solution. It is soluble in water, but is gradually hydrolysed in aqueous solution to form basic nitrate, which is also soluble : $Be(NO_3)_2+H_2O=Be(OH)NO_3+HNO_3$.

**Beryllium Sulphate,** $BeSO_4.4H_2O$, is obtained by dissolving BeO or $Be(OH)_2$ in hot conc. $H_2SO_4$ and cooling the resultant solution. It is a colourless, crystalline substance, soluble in water and hydrolysed in aqueous solution.

**Beryllium Acetate,** $Be_4O(CH_3COO)_6$, is prepared by dissolving $Be(OH)_2$ in acetic acid. The solution is evaporated to dryness, when the acetate is obtained as a white powder. It is a covalent compound and is insoluble in water, but soluble in organic solvents. It volatilises on strong heating. The acetate and other salts of beryllium with organic carboxylic acids, having the general composition, $Be_4O(OCOR)_6$, are complex compounds with more or less tetrahedral structures, in which the central oxygen atom is tetrahedrally surrounded by four Be atoms and each Be atom is surrounded by four oxygen atoms.

Other complexes of beryllium include fluoberyllates ($BeF_4^{2-}$), aquoberyllium salts, $[Be(H_2O)_4]^{++}$, etherates, alcoholates, the neutral complexes formed from β-diketones and β-ketoesters, such as acetyl acetone and ethyl acetoacetate, the anionic complex with benzoyl pyruvic acid *etc.* In all these complexes, beryllium exhibits quadricovalency.

**Tests** : (i) Beryllium is precipitated with aluminium in Group IIIA during qualitative analysis. The precipitates of $Be(OH)_2$ and $Al(OH)_3$ are soluble in excess of NaOH solution to form sodium beryllate and sodium aluminate respectively. On boiling the diluted solution, only $Be(OH)_2$ is thrown down as a white gelatinous precipitate. (ii) On adding ammonium carbonate soln. to a soln. of beryllium salts, beryllium carbonate is precipitated. The ppt. is soluble in excess of $(NH_4)_2CO_3$ soln., and the resultant soln. gives the ppt. of $Be(OH)_2$ on boiling. (iii) Be and Al can be separated by adding an acetic acid solution of 8-hydroxyquinoline (oxine) to a faintly acid solution of sodium aluminate and sodium beryllate, buffered with ammonium acetate-acetic acid. Aluminium is preciptated as oxinate, but beryllium remains in soln. Al-oxinate is separated by filtration, and $Be(OH)_2$ is precipitated from the filtrate by boiling it with $NH_4OH$.

Gravimetrically, Be is estimated as BeO by igniting the precipitated $Be(OH)_2$. It can also be weighed as the sulphate or pyrophosphate.

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## MAGNESIUM

*Symbol* : Mg ; *At. No.*=12 ; *At. Wt.*=24·32
*Electronic Configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2$
First isolated by Davy in 1808.

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**OCCURRENCE** : Magnesium does not occur native. In combination, the metal is found as **carbonates** in *Magnesite* ($MgCO_3$) and *Dolomite* ($MgCO_3.CaCO_3$) ; as **chlorides** and **sulphates** in *Stassfurt deposits, viz. Kieserite* ($MgSO_4.H_2O$), *Carnallite* ($KCl.MgCl_2.6H_2O$), *Kainite* ($MgSO_4.KCl.3H_2O$), *Schonite* ($K_2SO_4.MgSO_4.6H_2O$) ; as **silicates** in *Olivine* [$(Mg, Fe)_2SiO_4$], *Serpentine* ($3MgO.2SiO_2.2H_2O$), *Talc* ($3MgO, 4SiO_2.H_2O$), *Asbestos* [$CaMg_3(SiO_3)_4$], and as **oxide** in *Spinel* ($MgO.Al_2O_3$). **Epsom salt** ($MgSO_4.7H_2O$) and $MgCl_2$ occur in spring-water and sea-water. In the plant kingdom, magnesium is contained in the leaves as the green pigment, **chlorophyll.**

**Indian Ores** : In India, magnesium occurs as *magnesite* in Tamilnadu and Karnatak, and as *dolomite*, in many parts of the country, such as in Bihar, Orissa, West Bengal, Sikkim *etc*.

**EXTRACTION** : Magnesium is extracted either by the electrolytic reduction of fused magnesium chloride or by the chemical reduction of magnesium oxide.

(1) **Electrolytic process.**—In this process, anhydrous magnesium chloride, mixed with the chlorides of alkali- or alkaline earth metals, is used as the electrolyte.

Anhydrous magnesium chloride may be prepared by heating $MgCl_2.6H_2O$ or carnallite, first in presence of $NH_4Cl$ and finally in dry

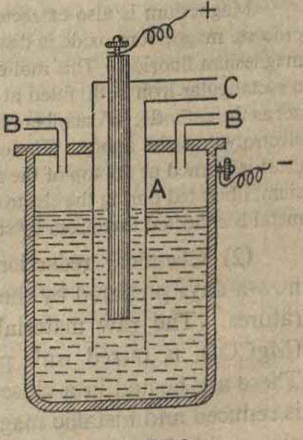


Fig. 13.2

hydrogen chloride (to prevent hydrolysis of $MgCl_2$). NaCl and $CaF_2$ are added to lower the melting point of the mixture and to minimise the formation of MgO at elevated temperatures.

The electrolyte is fused by heating to 700°C in a covered rectangular iron vessel which also serves as the cathode ; the anode consists of a graphite rod, surrounded by a porcelain pipe (A), which dips into the molten electrolyte. Some inert gas (coal-gas or $H_2$ ; nitrogen can not be used, as magnesium forms a nitride) is passed over the surface of the molten electrolyte through on opening (B), to prevent the oxidation of the liberated magnesium at the high temperature of the process. During electrolysis, chlorine gas is liberated at the anode and it goes out through the opening(C) of the porcelain tube. Magnisium, liberated at the cathode, is in the molten state and floats on the surface of the fused electrolyte, and is run off from time to time. [Fig. 13.2]

[It may be noted that magnesium is liberated in preference to sodium and calcium (from the added NaCl or $CaF_2$) so long as the amount of magnesium chloride is kept at a particular high level in the melt.]

In a similar process, magnesium is often extracted from anhydrous carnallite by using a layer of molten lead as cathode and graphite anode as above. The liberated metal forms an alloy with the molten lead cathode, and magnesium is obtained from this alloy by electrolysis of the same electrolyte is another cell where the alloy forms the anode and steel rods are used as the cathode.

Electrolysis of a solution of magnesium oxide in a molten mixture (1 : 1) of $MgF_2$ and $BaF_2$, (containing a little NaF to lower the melting point of the electrolyte), at 950°C is also used for the extraction of the metal. The electrolysis is carried out in a steel tank, having cast-iron rods fitted at the bottom to act as the cathode and suspended graphite anodes. The liberated magnesium, being lighter than the molten electrolyte, floats to the surface and is withdrawn from time to time from beneath the solid crust of the electrolyte.

Magnesium is also extracted *by the electrolysis of magnesium oxide.* In this process, magnesium oxide is dissolved in a molten mixture of sodium fluoride and magnesium fluoride. This molten mass, which is used as the electrolyte, is kept in a rectangular iron both, fitted at the bottom with a number of cast iron rods which act as the cathode. A number of stout graphite rods remain suspended in the molten electrolyte as the anode. The electrolysis is carried out at 900°—950°C. A hard crust is formed at the top of the molten electrolyte due to aerial cooling and magnesium, liberated during the electrolysis, is collected as a liquid below this crust. The metal is collected therefrom by suitable methods.

(2) **Chemical reduction : Carbothermal process.**—Magnesium is now-a-days prepared by the reduction of MgO by coke at high temperatures. The raw material, MgO, obtained by calcining magnesite ($MgCO_3$), is mixed with powdered coke and briquetted with pitch. These are heated in a closed electric furnace at about 2000°C. MgO is reduced and metallic magnesium in the form of vapour is produced along with CO : $MgO+C \rightleftharpoons Mg+CO$.

The mixture of the magnesium vapour and CO is quickly cooled to about 200°C by mixing with a large volume hydrogen or natural gas. [This prevents re-oxidation of the vapour of the metal during condensation.] Magnesium deposits in the form of powder (65% Mg and the rest MgO and C). The pure metal is obtained from this mixture by re-distillation under high vacuum at 800°C.

In the Canadian process the reduction of MgO is done by heating it with ferro-silicon at 1150°C under high vacuum. By this process the metal is obtained in a very high state of purity.

(3) **Extraction from Sea-water.**—Sea-water contains about 0.14% magnesium as chloride, bromide or sulphate. Sea-water is first concentrated to certain extent by aerial evaporation and is then treated with slaked lime to precipitate magnesium hydroxide : $MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2$. The precipitate is filtered, washed and dissolved in 10% HCl solution to convert it into magnesium chloride. [A little quantity of dil. $H_2SO_4$ is also added along with HCl to precipitate any calcium salt present, as insoluble $CaSO_4$.] The filtered solution of magnesium chloride is concentrated and cooled, when $MgCl_2.6H_2O$ crystallises out. The hydrated salt is partly dehydrated, fused with NaCl and electrolysed as stated in method (1), when magnesium metal is obtained.

**PROPERTIES :** Magnesium is a silvery white, light metal (m.p. 650°C ; sp. gr. 1.74). It is unaffected by dry air, but is attacked by moist air, forming a layer of MgO. It burns brilliantly with a dazzling flame when heated in air, forming the oxide, together with a little nitride ; $2Mg + O_2 = 2MgO$ ; $3Mg + N_2 = Mg_3N_2$. The metal has a great affinity for oxygen, and it burns even in $CO_2$, depositing carbon : $CO_2 + 2Mg = 2MgO + C$. It reduces many metallic and non-metallic oxides and chlorides at elevated temperatures. It combines directly with halogens, sulphur and nitrogen at high temperatures : $Mg + Cl_2 = MgCl_2$ ; $3Mg + N_2 = Mg_3N_2$. Cold water has no action on the metal, but it decomposes boiling water, liberating hydrogen ; the heated metal also burns in steam : $Mg + H_2O = MgO + H_2$. The metal is not acted upon by alkalis, but it readily dissolves in dilute acids (even very dil. $HNO_3$), to produce hydrogen : $Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$. Due to its stronger electropositive character, magnesium displaces many heavy metals from solutions of their salts : $2AgNO_3 + Mg = Mg(NO_3)_2 + 2Ag \downarrow$. Magnesium reacts with alkyl and aryl halides in dry ether medium to give alkyl (or aryl) magnesium halides or **Grignard reagents** : $RX + Mg \rightarrow RMgX$.

**Uses :** Magnesium is used for flash-light photography and for preparing military star-shells, light signals and fireworks. It is a constituent of many light alloys like magnelium (Al, 98% ; Mg, 2%) and electron (Mg, 95% ; Zn, 4.5% ; Cu, 0.5%), which are used for the construction of aeroplane and motor-car bodies. Some of the alloys of Mg are used as reducing agents in chemical laboratories. It is also an ingredient of incendiaries. Very pure metal is used for preparing Grignard reagents.

## COMPOUNDS OF MAGNESIUM.

**Magnesium hydride** (**$MgH_2$**) is obtained as a white solid by the action of $LiAlH_4$ on magnesium dialkyls. Direct combination of the two elements at high temperature and pressure also results in the formation of $MgH_2$. The substance is decomposed by water into $Mg(OH)_2$ and $H_2$.

$$MgH_2+2H_2O=Mg(OH)_2+2H_2\uparrow .$$

**Magnesium Oxide or Magnesia** (**MgO**) is prepared by heating the metal in air, or by the thermal decomposition of its carbonate, hydroxide or nitrate : $2Mg+O_2=2MgO$ ; $MgCO_3=MgO+CO_2$ ;

$$Mg(OH)_2=MgO+H_2O \text{ ; } 2Mg(NO_3)_2=2MgO+4NO_2+O_2.$$

Magnesium oxide is a white powder (m.p. 2800°C). It is a basic oxide, slightly soluble in water, the solution being alkaline in reaction. It dissolves in acids to form salt and water :

$$MgO+2HCl=MgCl_2+H_2O.$$

Magnesium oxide is used for making fire-bricks (for furnace lining) and crucibles. In admixture with asbestos, it is also used for insultating steam-pipes to prevent heat-radiation. Magnesia is a component of Sorel's cement, and is also used in medicine as an antacid.

**Magnesium Hydroxide, $Mg(OH)_2$,** is obtained by the interaction between a soluble hydroxide and a soluble magnesium salt : $MgSO_4+2NaOH=Mg(OH)_2+Na_2SO_4$. The precipitate is filtered, washed with water and dried at 100°C. [Heating above 100°C causes some decomposition to MgO.]

Magnesium hydroxide is a white powder, slightly soluble in water, imparting to it an alkaline reaction. It dissolves in ammonium chloride solution, due to the formation of slightly dissociated ammonium hydroxide in the equilibriated reaction, $Mg(OH)_2+2NH_4Cl\rightleftharpoons MgCl_2+2NH_4OH$. Magnesium hydroxide is used in medicine as an antacid and also in sugar industry.

**Magnesium Chloride, $MgCl_2$,** is prepared as the hexahydrate, $MgCl_2.6H_2O$, by dissolving the metal or its oxide, hydroxide or carbonate in dilute HCl, and concentrating the solution to crystallisation : $Mg+2HCl=MgCl_2+H_2$ ; $MgCO_3+2HCl=MgCl_2+CO_2+H_2O$. The hexahydrate is obtained on a large scale from carnallite. When carnallite is fused, most of the potassium chloride remains as solid. On cooling the melt, the remaining KCl crystallises out, leaving the fused $MgCl_2.6H_2O$. Potassium chloride is removed and the melt is further cooled to solidify, when $MgCl_2.6H_2O$ is obtained. The anhydrous salt cannot be prepared by heating the hydrated one. On heating $MgCl_2.6H_2O$, basic magnesium chloride, $MgO.MgCl_2$ is first formed, and finally, complete decomposition to MgO takes place. The interaction between the water from the hydrate and $MgCl_2$ is responsible for this hydrolytic decomposition :

$$MgCl_2+H_2O \rightleftharpoons MgO+2HCl.$$

[$MgCl_2$ is only slightly hydrolysed in solution under ordinary conditions, but extensive hydrolysis takes place under more drastic conditions, *i.e.* on heating.]

Anhydrous $MgCl_2$ may, however, be prepared by heating the hydrated salt in a current of dry hydrogen chloride gas, or by heating the double salt, ammonium magnesium chloride ($MgCl_2.NH_4Cl.6H_2O$), or by heating a mixture of MgO and coke in a current of $Cl_2$ :

$MgCl_2.NH_4Cl.6H_2O = MgCl_2+NH_4Cl+6H_2O$ ; $MgO+C+Cl_2 = MgCl_2+CO$.

Magnesium chloride is a colourless, crystalline, deliquescent solid. It is highly soluble in water and is slightly hydrolysed in solution at ordinary temperatures. The hydrate ($MgCl_2.6H_2O$), however, undergoes hydrolysis on heating in air, forming basic magnesium chloride first and ultimately MgO. A concentrated solution of $MgCl_2$ dissolves MgO, and the solution soon sets to a hard mass (*Sorel's cement*).

Magnesium chloride is used in the preparation of Sorel's cement which is used for dental stoppings, for cementing glass and porcelain and as a finish for plasters. It is also used for lubricating cotton threads during spinning.

**Magnesium Perchlorate, $Mg(ClO_4)_2$,** is prepared by dissolving MgO, $Mg(OH)_2$ or $MgCO_3$ in perchloric acid and crystallising the product, when the hexahydrate, $Mg(ClO_4)_2.6H_2O$, separates out. The anhydrous salt is obtained by heating the hydrated salt at 250°C. It is a white powder and is mainly used as a strong desiccant under the name, *anhydrone*.

**Magnesium Fluoride, $MgF_2$,** is formed as a white solid, insoluble in water and dil. acids, by the action of hydrofluoric acid on MgO, $Mg(OH)_2$ or $MgCO_3$.

**Magnesium Bromide, $MgBr_2.6H_2O$,** occurs in small quantities in sea-water and it serves as a source for the preparation of bromine. It is formed by the direct union of the elements at elevated temperatures, or by heating a mixture of MgO and C in a stream of bromine vapour. It resembles $MgCl_2$ in its properties.

**Magnesium Iodide, $MgI_2.8H_2O$,** is prepared as a white hygroscopic solid, by the reaction of HI on MgO, and crystallising the product from solution.

**Magnesium Nitrate, $Mg(NO_3)_2.6H_2O$,** is prepared by dissolving MgO or $MgCO_3$ in dilute $HNO_3$ and evaporating the solution to crystallisation : $MgO+2HNO_3=Mg(NO_3)_2+H_2O$.

Magnesium nitrate forms colourless, crystalline and very deliquescent crystals. The dehydration of the hydrated salt is attended with some decomposition. It is highly soluble in water, when slight hydrolysis occurs. On heating strongly, it decomposes into MgO, $NO_2$ and $O_2$ : $2Mg(NO_3)_2=2MgO+4NO_2+O_2$.

**Magnesium Sulphate, $MgSO_4$,** occurs as the mineral Kieserite ($MgSO_4.H_2O$) and also in some spring-water. It can be prepared by dissolving Magnesite ($MgCO_3$) in hot, dilute $H_2SO_4$ and crystallising the salt from the solution, or by dissolving Dolomite ($CaCO_3.MgCO_3$) in hot, dilute $H_2SO_4$, filtering off the precipitated calcium sulphate and crystallising the salt from the filtrate. It crystallises out as the heptahydrate, $MgSO_4.7H_2O$, known as **Epsom salt.** On a large scale, the Epsom salt is prepared by dissolving Kieserite in hot water (the mineral is practically insoluble in cold water), filtering the solution and then concentrating the clear filtrate to crystallisation.

Magnesium sulphate is obtained as colourless crystals, commonly with 7 molecules of water of crystallisation. It is soluble in water. Many other hydrates are known (with 12, 5, 4 and 1 $H_2O$). On heating, the heptahydrate slowly loses water and the anhydrous salt is formed at about 200°C. At higher temperatures, the salt is partly decomposed, forming MgO and $SO_3$ : $MgSO_4=MgO+SO_3$.

Magnesium sulphate is used in paper industry, in dyeing and tanning, in dressing cotton and silk goods and in the manufactrue of paints and soaps. It is also used as a fire-proofing agent. The salt is used in medicine as a purgative. Platinised magnesium sulphate is used as a catalyst in the manufacture of sulphuric acid.

**Magnesium Carbonate, $MgCO_3$,** occurs in nature as Magnesite ($MgCO_3$), and with calcium carbonate, as Dolomite ($CaCO_3.MgCO_3$). It can be obtained as a precipitate by adding a solution of sodium bicarbonate to a solution of a magnesium salt.

Basic magnesium carbonate [$MgCO_3.Mg(OH)_2.3H_2O$] is obtained, if a solution of sodium carbonate is used in the preparation. (This is due to the extensive hydrolysis of $Na_2CO_3$ in aqueous solution, forming $OH^-$ ions.) The normal carbonate is obtained from the basic salt in the following ways :

Through a suspension of the basic carbonate in water, excess of $CO_2$ is passed, when the suspension dissolves, forming magnesium bicarbonate in solution. The solution, on boiling, precipitates $MgCO_3$.

Magnesium carbonate is a water-insoluble white powder, but it dissolves in dilute acids with effervescence, giving off $CO_2$ and forming the salts of the corresponding acids : $MgCO_3+2HCl=MgCl_2+CO_2+H_2O$. It slowly reacts with water containing dissolved $CO_2$ to form the soluble magnesium bicarbonate :

$$MgCO_3+CO_2+H_2O=Mg(HCO_3)_2.$$

Magnesium carbonate is largely used in the preparation tooth-powder and tooth-pastes. It is also used as the starting material for the preparation of MgO and some other magnesium salts.

**Magnesium Bicarbonate,** $Mg(HCO_3)_2$, is formed in solution by the action of $CO_2$ and water on $MgCO_3$. Being an unstable compound, it readily decomposes into $MgCO_3$, $CO_2$ and $H_2O$ on heating the solution :

$$Mg(HCO_3)_2\rightleftharpoons MgCO_3+CO_2+H_2O.$$

**Magnesium Nitride,** $Mg_3N_2$, is obtained as a light yellow crystalline substance on passing nitrogen or $NH_3$ over red-hot magnesium powder. The product is decomposed on heating with water to form $NH_4OH$ and $Mg(OH)_2$ : $Mg_3N_2+8H_2O=3Mg(OH)_2+2NH_4OH$.

The reaction of the formation of $Mg_3N_2$ is used to remove $N_2$ during the isolation of inert gases from air.

**Magnesium Phosphate.**—Different types of magnesium phosphates are known. The normal phosphate, $Mg_3(PO_4)_2$, occurs in animal bones and in many seeds. It is obtained by adding calculated amount of $Na_2HPO_4$ to a moderately concentrated solution of magnesium sulphate (containing a little amount of $NaHCO_3$). But, on adding excess of $Na_2HPO_4$ to a solution of magnesium salt, the magnesium hydrogen phosphate, $MgHPO_4$, is generally precipitated. On heating the precipitated $MgHPO_4$, it decomposes to form the normal phosphate and the acid phosphate, $Mg(H_2PO_4)_2$ :

$$4MgHPO_4=Mg_3(PO_4)_2+Mg(H_2PO_4)_2.$$

The acid salt, $Mg(H_2PO_4)_2$ is also formed on heating MgO with conc. $H_3PO_4$ : $MgO+2H_3PO_4=Mg(H_2PO_4)_2+H_2O$.

When $Na_2HPO_4$ is added to a solution of a magnesium salt in presence of $NH_4OH$ and $NH_4Cl$, magnesium ammonium phosphate, $Mg(NH_4)PO_4.6H_2O$, a sparingly soluble crystalline compound, is precipitated. $MgCl_2+NH_4OH+Na_2HPO_4=Mg(NH_4)PO_4\downarrow+2NaCl+H_2O$. [This reaction is used in the detection and estimation of the metal.] The precipitate decomposes on strong heating to give magnesium pyrophosphate, $Mg_2P_2O_7$ ; $2Mg(NH_4)PO_4 \rightarrow Mg_2P_2O_7 + H_2O + 2NH_3 \uparrow$.

**Tests** : (i) When a magnesium salt, mixed with dry $Na_2CO_3$, is heated on a charcoal block under the reducing flame, a white incandescent mass is left. This, on moistening with a drop of dilute cobalt nitrate solution and re-heating in the oxidising flame, produces a pink colour. (ii) Solutions of NaOH or $NH_4OH$ precipitate $Mg(OH)_2$ from a solution of magnesium salt. The white precipitate dissolves on boiling with ammonium chloride solution. (iii) A solution of disodium hydrogen phosphate, when added to an ammoniacal solution (containing ammonium chloride) of a magnesium salt, gives a crystalline white precipitate of magnesium ammonium phosphate [$Mg(NH_4)PO_4$].

Gravimetrically, magnesium is estimated as magnesium pyrophosphate, by igniting $Mg(NH_4)PO_4$. It is also weighed as oxinate, $Mg(C_9H_6ON)_2.2H_2O$ after drying at 100°C. Volumetrically, it may be estimated with E.D.T.A. solution.

## CALCIUM

*Symbol* : Ca ; *Atomic No.*=20 ; *Atomic Wt.*=40.0
*Electronic configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
[First isolated by Davy (1808)]

**Occurrence** : Due to its very reactive nature, calcium is not found native. Calcium minerals are, however, very widely distributed in nature. The important minerals of calcium are : (i) the carbonates, **Limestone, Chalk, Calcite, Marble ($CaCO_3$)** and **Dolomite ($CaCO_3.MgCO_3$)**, (ii) the sulphate, **Anhydrite ($CaSO_4$)** and **Gypsum ($CaSO_4.2H_2O$)**, (iii) the fluoride, **Fluorspar ($CaF_2$)**, (iv) the phosphates, **Phosphorite [$Ca_3(PO_4)_2$]** and **Apatite [Fluor-apatite, $3Ca_3(PO_4)_2.CaF_2$** and **Chlor-apatite, $3Ca_3(PO_4)_2.CaCl_2$.]** and (v) the silicate, **Felspar ($CaAl_2Si_2O_8$)**. Calcium is an important constituent of bones, teeth, egg-shells, corals, oysters, conch-shells etc. About 5% of earth's crust consist of calcium compounds.

**Indian Ores** : In India, calcium is found as *Marbles* in Jabbalpur (Madhya Pradesh), Jodhpur (Rajasthan), Himachal Pradesh ; as *limestone* in Madhya Pradesh, Orissa, Bihar, Khasi and Jayanti Hills ; as *Gypsum* in Rajathan ; as *Fluorspar* in Madhya Pradesh and Rajasthan and as *Dolomite* in Orissa and Bihar.

**Extraction** : Calcium is extracted by the electrolysis of fused calcium chloride, mixed with some calcium fluoride (16.5%) to lower its melting point to about 664°C.

$$CaCl_2 \rightleftharpoons Ca^{++} + 2Cl^-$$

$$Ca^{++}+2e \rightarrow Ca \text{ (at the cathode)}$$
$$2Cl^{-}+2e \rightarrow Cl_2 \text{ (at the anode).}$$

[$CaCl_2$ is prepared by dissolving limestone or marble ($CaCO_3$) in dilute HCl and heating the resultant solution to obtain dry calcium chloride.]

The electrolysis is carried out at 700°C in a graphite cell which is covered inside by a layer of the solidified melt. The graphite-plate lining of the cell acts as the anode and the cathode is awater-cooled iron rod, which just dips in the fused electrolyte (Fig.13.3). During electrolysis, calcium is deposited at the cathode as a solid (m.p. 851°C) and chlorine is liberated at the anode. The cathode is slowly raised out of the melt by an electrically driven mechanism, as the metal starts depositing on it, so that the metal is obtained in the form of a rod, which is protected from aerial oxidation by coating of the melt. (The metal rod, so formed, acts as the cathode.) The metal is finally freed from calcium chloride by sublimation in vacuum.

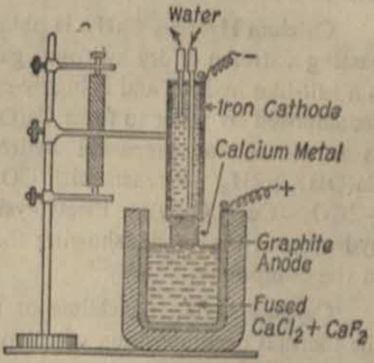


Fig. 13.3

Calcium can also be obtained by the carbothermal reduction of CaO, as described for magnesium.

The pure metal may be prepared by heating pure calcium chloride with aluminium, and volatilising the aluminium chloride formed :

$$3CaCl_2+2Al = 3Ca+Al_2Cl_6.$$

**Properties :** Calcium is a very reactive, silver-white, soft and light metal (m.p. 851°C, sp. gr. 1.54). It is unaffected by dry air, but in contact with moist air, it gradually tarnishes, forming calcium hydroxide, which combines with $CO_2$ of air to form calcium carbonate. It readily reacts with water to form $H_2$ and $Ca(OH)_2$ : $Ca+2H_2O=Ca(OH)_2+H_2$. It burns when heated in air, forming calcium oxide and nitride : $2Ca+O_2=2CaO$ ; $3Ca+N_2$ (from air)$=Ca_3N_2$. It also reacts with carbon at high temperature to form calcium carbide : $Ca+2C=CaC_2$. Calcium reduces many metallic oxides at elevated temperatures, and also reacts with chlorine and sulphur, when heated, to form the chloride and the sulphide :

$MO+Ca=M+CaO$ ; $Ca+Cl_2=CaCl_2$ ; $Ca+S=CaS$.
(M=a bivalent metal.)

Calcium liberates hydrogen on reacting with dilute mineral acids (except $HNO_3$). The metal absorbs gaseous ammonia at ordinary temperatures.

Metallic calcium is used for drying alcohol. It is also used as a de-oxidant in metal castings in removing last traces of nitrogen (or air), in the isolation of argon and in preparing calcium hydride.

## COMPOUNDS OF CALCIUM.

**Calcium Hydride, $CaH_2$,** is obtained as a white crystalline solid by passing a stream of dry hydrogen gas over molten calcium (500°C). It is a salt-like hydride and is highly reducing in character. It is readily decomposed by water to form $Ca(OH)_2$ and $H_2$ and as such, it is used as a source for preparing hydrogen (*hydrolith*) : $CaH_2+2H_2O=Ca(OH)_2+2H_2$. It reacts with $CO_2$ to form calcium formate : $CaH_2+2CO_2=Ca(H.COO)_2$. Electrolysis of the fused compound produces hydrogen at the anode, showing the presence of negative hydride ion in the compound.

**Calcium Oxide, Quicklime or Lime, (CaO),** may be prepared by the thermal decomposition of calcium nitrate : $2Ca(NO_3)_2=2CaO+4NO_2+O_2$. But, it is usually prepared, in the laboratory or on a large scale, by the thermal dissociation of calcium carbonate : $CaCO_3 \rightleftharpoons CaO+CO_2-42.5$ Kcal. In the actual industrial process, this reversible reaction is virtually led to completion, by carrying out the thermal decomposition in a vertical shaft-furnace, called the lime-kiln. The furnace is a tall brick-built structure, having a door at the top for charging limestone. Heating is done by burning producer gas, introduced at the bottom or by the burning of coal mixed with the limestone inside the furnace. Temperature of about 1000°C is attained, when limestone is decomposed into

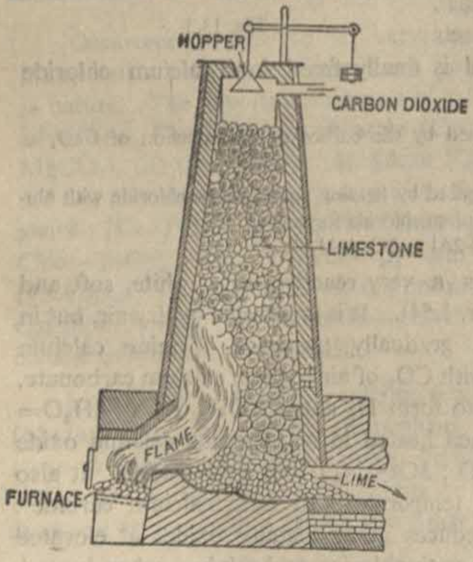


Fig. 13.4

$CaO$ and $CO_2$. Lime gradually makes it way down the kiln and is taken out through an opening at the base and $CO_2$ passes out through an exit pipe near the top. The process is continuous.

Quicklime is formed as hard, white, amorphous lumps, melting at 2576°C. When heated, it becomes incandescent and emits an intense brilliant white light, called *lime light*. Quicklime absorbs moisture and $CO_2$ from air to give a mixture of calcium hydroxide and calcium carbonate. The hydroxide, however, absorbs more $CO_2$ from air, so that the ultimate product is calcium carbonate : $CaO+H_2O=Ca(OH)_2$ ; $CaO+CO_2=CaCO_3$ ; $Ca(OH)_2+CO_2=CaCO_3+H_2O$.

Calcium oxide vigorously reacts with water with a hissing sound, with the evolution of much heat. As a result, a portion of water is transformed into steam. The lumps of CaO swell up, crack and fall into a white powder, forming calcium hydroxide. This phenomenon is known as the **slaking of lime** : $CaO+H_2O=Ca(OH)_2$ ; the calcium hydroxide, thus formed, is known as **slaked lime.** Calcium oxide is a basic oxide. It reacts with acids to form the corresponding calcium salts and water : $CaO+2HCl=CaCl_2+H_2O$. With acidic oxides like $SiO_2$ and $P_2O_5$, it forms infusible calcium silicate and calcium phosphate respectively : $CaO+SiO_2=CaSiO_3$ ; $3CaO+P_2O_5=Ca_3(PO_4)_2$. Ammonium salts, when heated with CaO, liberate ammonia : $2NH_4Cl+CaO=CaCl_2+H_2O+2NH_3\uparrow$. On heating with carbon at high temperatures in an electric furnace, CaO forms calcium carbide : $CaO+3C=CaC_2+CO$. It reacts with $Cl_2$ above 300°C to give $CaCl_2$ and oxygen : $2CaO+2Cl_2=2CaCl_2+O_2$.

Quicklime is largely used for the manufacture of calcium carbide and slaked lime. As a basic flux, it is used in metallurgy. In chemical laboratories, calcium oxide is used for drying alcohols and ammonia gas.

**Calcium Peroxide ($CaO_2$)** is obtained as white crystals ($CaO_2.8H_2O$), on adding $H_2O_2$ solution to lime water. The anhydrous $CaO_2$ may be prepared by heating the hydrate gently. On strong heating, it decomposes to CaO and $O_2$. It is used as an antiseptic.

**Calcium Hydroxide, Slaked lime, [$Ca(OH)_2$],** is generally prepared by slaking quicklime with water. It is also formed by the action of a solution of NaOH on a concentrated solution of a calcium salt :

$$CaCl_2+2NaOH=Ca(OH)_2+2NaCl.$$

Calcium hydroxide is an amorphous white powder, slightly soluble in water. The solution is called *lime water*. When the added calcium hydroxide to the solution exceeds its solubility in water, a suspension of the hydroxide in lime water is obtained, which is known as *milk of lime.* Calcium hydroxide is decomposed above 100°C to CaO and water : $Ca(OH)_2 = CaO + H_2O$.

A solution of $Ca(OH)_2$ in water (lime water) absorbs $CO_2$ from air, forming a thin crust of $CaCO_3$ on the surface. When $CO_2$ is passed into lime water, a white precipitate of $CaCO_3$ is first formed, which dissolves, on passing excess of $CO_2$, to form a clear solution of calcium bicarbonate, $[Ca(HCO_3)_2]$. The solution of calcium bicarbonate precipitates $CaCO_3$ again on heating : $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$ ; $CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$ ; $Ca(HCO_3)_2 \xrightarrow{heat} CaCO_3 + CO_2 + H_2O$. Dry slacked lime absorbs chlorine gas (at 40°C) to form bleaching powder :

$$Ca(OH)_2 + Cl_2 = H_2O + Ca(OCl)Cl \text{ (bleaching powder).}$$

Slaked lime is used in the manufacture of caustic soda, bleaching powder, glass, superphosphate of lime *etc.* It is also used for the recovery of $NH_3$ in the Solvay process for the manufacture of $Na_2CO_3$, for softening hard water, for removing hair from hides in tanning, for the purification of coal-gas, for the manufacture of mortar and plaster and for white-washing of buildings.

**Sodalime** is a solid mixture of $Ca(OH)_2$ and NaOH. It is obtained by slaking quicklime with caustic soda solution and heating the mixture to dryness. It is used as a desiccating agent, as a reagent for absorbing $CO_2$, and in the laboratory preparation of some hydrocarbons.

**Calcium Fluoride, $CaF_2$,** occurs in nature as *fluorspar* or *fluorite*. It can be prepared by dissolving the metal, its oxide, hydroxide or carbonate in hydrofluoric acid, or by adding a solution of sodium fluoride to a solution of calcium salt in water. It is also formed on fusing lime or calcium carbonate with solid sodium fluoride, and dissolving out the resultant $Na_2CO_3$ with water.

Calcium fluoride is a white solid, practically insoluble in water and dilute acids. On melting, it forms a white opaque mass like enamel.

It is used as flux in metallurgy. It also finds application in the manufacture of enamel, glazes, glass and also for the preparation of fluorine and its compounds. Transparent fluorspar or fluorite is used for preparing optical lenses.

**Calcium Chloride, ($CaCl_2$),** is obtained as a by-product during the manufacture of $Na_2CO_3$ by the Solvay process. It is prepared by dissolving CaO, $Ca(OH)_2$ or $CaCO_3$ in hydrochloric acid. The solutions are evaporated to crystallisation, when $CaCl_2.6H_2O$ crystals are obtained : $CaO + 2HCl = CaCl_2 + H_2O$ ; $Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$ ; $CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$.

The hexahydrate loses water on heating to form $CaCl_2.2H_2O$ first and ultimately the anhydrous salt, above 260°C. The anhydrous salt melts on heating to 773°C. The hexahydrate of the salt is a colourless, crystalline, highly deliquescent solid. The anhydrous salt is very hygroscopic. It forms an adduct, $CaCl_2.8NH_3$, with ammonia, and $CaCl_2.\ 6C_2H_5OH$ with ethyl alcohol. It is soluble in water with slight hydrolysis : $CaCl_2+2H_2O \rightleftharpoons Ca(OH)_2+2HCl$.

Anhydrous fused calcium chloride is used as a desiccating agent. ($NH_3$ gas and alcohol can not be dried with it.) The hydrated salt is used in refrigeration and in making freezing mixtures.

**Calcium bromide** and **Calcium iodide** can be prepared by methods similar to that of $CaCl_2$. Both of them form hexahydrate. They resemble each other and also calcium chloride in their properties.

**Bleaching powder** : When moderately dry slaked lime is treated with chlorine in the cold, it absorbs about 35-36% of the gas to form a dry white powder, which possesses bleaching and disinfecting properties. This white powder is known as **bleaching powder** or **chloride of lime.**

For the manufacture of bleaching powder, the lime should be as pure as possible and it is passed through a sieve before use. It should contain about 4 %more water than corresponds to the formula $Ca(OH)_2$, as perfectly dried lime does not absorb chlorine at all. The chlorine gas used should be cool and dry and should be freed from HCl as far as possible.

Two different processes are followed for the manufacture of bleaching powder. With concentrated electrolytic chlorine, the manufacture is carried out in large closed *chlorine chambers*, in which the slaked lime is spread on the floor in 3-4 inch-layers which are raked into furrows for the exposure of larger surface. Stream of chlorine is led into the chambers through a pipe placed at one end near the roof, and being a heavy gas, it sinks downwards, and is at first rapidly absorbed by lime. Later, the absorption becomes slow and the temperature rises. Care should be taken to maintain the temperature below 25°C, and too much use of chlorine should be avoided. After introducing the proper amount of chlorine, the chambers are closed and allowed to stand for about 24 hours, during which, layers of lime are turned over to expose fresh surfaces. . After the scheduled time, the last traces of chlorine are sucked out by passing excess of air through the chambers, and the product is collected.

With diluted chlorine, the manufacture of bleaching powder is carried out in **Hasenclever's Cylinder apparatus** (Fig. 13.5) which consists of six to eight horizontal cast-iron cylinders, lying one above the other, and each fitted inside (along its length) with a rotating shaft provided with blades. Each shaft is connected with a toothed-wheel system and is kept revolving slowly. The uppermost cylinder is provided with a feeding hopper to introduce slaked lime. The adjoining cylinders have an opening at one end for the passage of the charge from the upper to the next lower one. Chlorine gas is introduced through an inlet at one end of the lowermost cylinder, which is also provided with an outlet for removing the finished product. Slaked lime, fed at the uppermost cylinder, gradually move downwards, (passing from one end to the other in one cylinder and in an opposite direction in the next one), travels a long zig-zag course, where it meets the stream of chlorine moving upwards in the opposite direction. The gas is all absorbed by the lime and the absorption is facilitated by the exposure of fresh surfaces of lime by the rotating blades. The waste gas, escaping through an outlet at the top, is practically free from chlorine. The bleaching powder is let out at the bottom from time to time into wooden casks situated below.

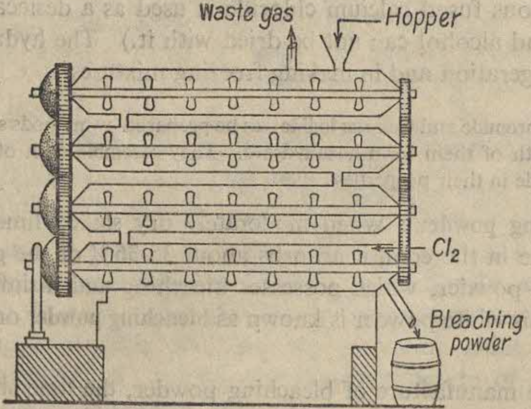


Fig. 13.5

Bleaching powder is an unstable compound, smelling strongly of chlorine. It is decomposed by moisture and $CO_2$ of air. It is completely decomposed by acids, and even by moist $CO_2$ at 70°C :
$Ca(OCl)Cl+HCl=CaCl_2+HOCl$ ; $HOCl+HCl=H_2O+Cl_2\uparrow$ .
Commercial bleaching powder contains some unchanged $Ca(OH)_2$. The bleaching power of bleaching powder depends upon the amount of *available* chlorine contained in it. A good quantity of commercial

material contains about 38% *available* chlorine. It is estimated by treating a known weight of bleaching powder sample with acetic acid and reacting the evolved $Cl_2$ with KI solution. Equivalent amount of iodine is set free from KI solution and this is estimated by titrating with standard sodium thiosulphate solution. From the amount of $I_2$ liberated, the chlorine-content of the sample is computed.

$Ca(OCl)Cl+2HAc+2KI=CaCl_2+2KAc+I_2+H_2O$ ;
$I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$. (Ac=acetate radical)

Bleaching powder is not easily soluble in water, but on heating with water, it forms a solution containing calcium chloride and calcium hypochlorite : $2Ca(OCl)Cl=Ca(OCl)_2+CaCl_2$.

It is a strong oxidising agent and oxidises PbO to $PbO_2$ and MnO to $MnO_2$. It reacts with strong ammonia solution to evolve nitrogen :

$$3Ca(OCl)Cl+2NH_4OH=3CaCl_2+N_2+5H_2O.$$

Sodium carbonate reacts with bleaching powder to form calcium carbonate, sodium chloride and sodium hypochlorite :

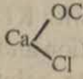
$$Ca(OCl)Cl+Na_2CO_3=CaCO_3+NaOCl+NaCl.$$

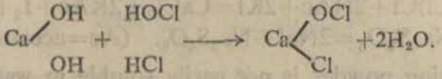
It liberates iodine from an acidified solution of potassium iodide : $Ca(OCl)Cl+2KI+2HCl=CaCl_2+2KCl+H_2O+I_2$. When boiled in presence of a little cobalt salt (catalyst), a solution of bleaching powder evolves oxygen : $2Ca(OCl)Cl=2CaCl_2+O_2$.

The bleaching action of bleaching powder is due to the ease with which chlorine is set free on treating this substance with dilute acids. In the first stage, hypochlorous acid is formed, which is then acted upon by the acids to set free nascent oxygen, which actually performs the bleaching.

Bleaching powder is extensively used for bleaching paper and textile materials. It is also used as a disinfectant, deodorant, germicide and as a sterilizing agent. It is also largely used for the manufacture of chlorine and chloroform.

**Composition and Formula of Bleaching Powder** : The commercial bleaching powder of good quality contains about 38% available chlorine, and its composition corresponds approximately to $3Ca(OCl)Cl.Ca(OH)_2.5H_2O$. The correct formula of bleaching powder was a matter of much controversy, and from time to time, many chemists suggested various formulas to represent the compound. Balard suggested the formula $Ca(OCl)_2.CaCl_2$ for bleaching powder. Such a formula should contain considerable proportion of free $CaCl_2$. But, the extracts of bleaching powder with water or alcohol (in both of which $CaCl_2$ is freely soluble) contained much less chlorine (as chloride). So, this formula is not tenable. Stahlschmidt put forward the formula Ca(OH)OCl for bleaching powder. Such a formula seems to be incorrect due to the fact that a good quality bleaching powder contains as much as

39% available chlorine, but Stahlschmidt's formula cannot account for the existence of more than 33% available chlorine in bleaching powder. Odling represented bleaching powder by the formula  $Ca\begin{matrix}OCl\\Cl\end{matrix}$, *i.e.* as **calcium chlorohypochlorite,** which is formed from a molecule of $Ca(OH)_2$ by the simultaneous action of 1 molecule each of HCl and HOCl :



$$Ca\begin{matrix}OH\\OH\end{matrix} + \begin{matrix}HOCl\\HCl\end{matrix} \longrightarrow Ca\begin{matrix}OCl\\Cl\end{matrix} + 2H_2O.$$

Detailed chemical analysis of bleaching powder by various workers pointed to the correctness of Odling's formula for bleaching powder and as such, bleaching powder is now accepted as calcium chlorohypochlorite.

**Calcium Nitride** ($Ca_3N_2$) is obtained as a white solid on heating metallic calcium in nitrogen gas at 440°C. It is hydrolysed, on boiling with water, to form ammonia and calcium hydroxide : $Ca_3N_2+6H_2O=3Ca(OH)_2+2NH_3$.

**Calcium Nitrate,** $[Ca(NO_3)_2]$, may be prepared by the action of dilute $HNO_3$ on lime, chalk or marble, and evaporating the resultant solutions to crystallisation. It is manufactured by the action of $HNO_3$ on limestone : $CaCO_3+2HNO_3=Ca(NO_3)_2+CO_2+H_2O$.

It forms colourless, deliquescent crystals, $[Ca(NO_3)_2.4H_2O]$, which are highly soluble in water. On strong heating, it decomposes into lime, $NO_2$ and oxygen : $2Ca(NO_3)_2=2CaO+4NO_2+O_2$.

Calcium nitrate is used as a fertilizer, specially in the form of nitro-lime (a mixture of lime and calcium nitrate).

**Calcium Sulphide, CaS,** may be prepared by reducing calcium sulphate with coke at 900°C : $CaSO_4+4C=CaS+4CO$. It is also formed when lime is heated in $H_2S$ gas : $Ca(OH)_2+H_2S=CaS+2H_2O$. It is obtained as a by-product in the LeBlanc process of manufacturing sodium carbonate.

Calcium sulphide is sparingly soluble in water and is hydrolysed by it : $2CaS+2H_2O=Ca(OH)_2+Ca(HS)_2$. It is used in luminous paints.

**Calcium Sulphate** ($CaSO_4$) occurs in nature as **Anhydrite** ($CaSO_4$) and **Gypsum** ($CaSO_4.2H_2O$). It can be prepared as the sparingly soluble dihydrate, $CaSO_4.2H_2O$, by the reaction between solutions of a soluble sulphate and a calcium salt : $CaCl_2+2H_2O+Na_2SO_4=(CaSO_4, 2H_2O)+2NaCl$. It can also be obtained by the action of dilute $H_2SO_4$ on powdered lime, chalk or marble :

$$CaCO_3+H_2SO_4+H_2O=(CaSO_4.2H_2O)+CO_2.$$

Calcium sulphate is a crystalline white powder, sparingly soluble in water. It dissolves in ammonium sulphate solution, due to the formation of complex ions. The dihydrate, $CaSO_4.2H_2O$ (gypsum), on heating to 120°—130°C, loses water to form the hemi-hydrate, $2CaSO_4.H_2O$, which is commonly known as the **Plaster of Paris** : $2(CaSO_4.2H_2O) \rightleftharpoons 2CaSO_4.H_2O+3H_2O$.

Plaster of Paris is manufactured by heating gypsum in large steel drums, fitted with stirrers, or in rotary kilns. The gypsum used for the purpose should be free from any carbonaceous or other reducing impurities. Contamination with carbonaceous fuels during heating should also be avoided. Otherwise, $CaSO_4$ is reduced during heating to CaS. When water is added to Plaster of Paris, the reverse change of hydration occurs and gypsum is re-formed as a mass of interlacing crystals which set to a hard mass. On heating the dihydrate above 200°C, the anhydrous salt is formed (the gypsum is then said to be *dead-burnt*), which does not set as Plaster of Paris. The anhydrous salt decomposes above 400°C to CaO and $SO_3$.

Gypsum ($CaSO_4.2H_2O$) is used in the manufacture of Plaster of Paris, ammonium sulphate (fertilizer), glazed paper, chalk-pencils *etc.* Plaster of Paris is used in surgical bandages, for making moulds in pottery work and ornamental castings, for preparing statues and also as a cement and wall-plaster.

**Calcium Carbonate, ($CaCO_3$),** occurs in nature as *marble, limestone, chalk, Iceland spar etc.* In combination with $MgCO_3$, it occurs as *dolomite.* Coral, egg-shell, conch-shell, oyster-shell and bones also contain large amounts of calcium carbonate. It may be prepared by the action of $CO_2$ on quicklime or slaked lime : $Ca(OH)_2+CO_2=CaCO_3+H_2O$. It is also precipitated as a white powder (known as *precipitated chalk*), when a solution of $Na_2CO_3$ or $(NH_4)_2CO_3$ is added to a solution of calcium salt : $CaCl_2+Na_2CO_3=CaCO_3\downarrow+2NaCl$.

Calcium carbonate is a white solid, which is practically insoluble in water. It dissolves in acids to form calcium salts and carbon dioxide : $CaCO_3+2HCl=CaCl_2+CO_2+H_2O$. It decomposes into calcium oxide and carbon dioxide on strong heating : $CaCO_3 \rightleftharpoons CaO+CO_2$. When a stream of $CO_2$ gas is bubbled through a suspension of finely divided calcium carbonate in water, the latter dissolves, forming calcium bicarbonate in solution. The clear solution, however, forms a white precipitate of calcium carbonate on heating : $CaCO_3+CO_2+H_2O \rightleftharpoons Ca(HCO_3)_2$.

Limestone is the starting material for the production of lime. It is also used in large quantities in the manufacture of cement and glass. It is applied as a flux in some metallurgy. Marble is used in making statues and buildings and for the preparation of $CO_2$ in laboratories. Chalk is used in *whiting*. Precipitated chalk is used in face-powder, tooth-powder and tooth-pastes, and as an antacid in medicine.

**Calcium Carbide, $CaC_2$,** is manufactured by heating a mixture of coke and quicklime (in the ratio 2 : 3) in an electric furnace at a temperature above 2000°C : $CaO+3C=CaC_2+CO\uparrow$. The furnace used is a rectangular fireclay tank with gas-carbon lining and graphite base. (Fig. 13.6) The charge is loaded in the furnace and a thick carbon rod, suspended vertically from above and connected to the source of electricity, is introduced in the furnace to strike an arc. High temperature is produced, which brings about the above reaction, and the molten mass of the product is withdrawn from the furnace by tapping off after the reaction is complete. The molten mass is cooled and the big solid lumps are broken down into small pieces by crushers. It is stored in air-tight iron drums.

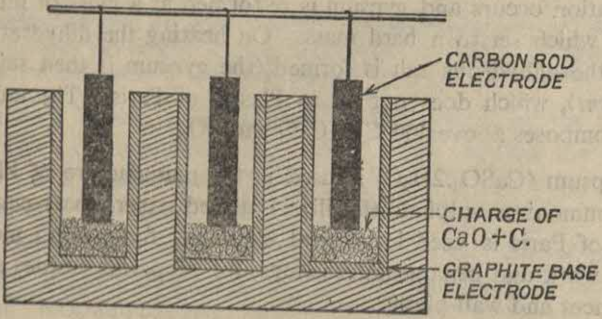


Fig. 13.6

Calcium carbide of commerce is available in more or less white hard lumps, having foul smell. It reacts with water to form acetylene, and is industrially used as a source of this gas :

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2\uparrow .$$

When heated in a stream of nitrogen in presence of a small quantity of calcium chloride, it forms calcium cyanamide :

$$CaC_2+N_2=CaNCN+C.$$

Calcium carbide is used for the manufacture of acetylene gas and calcium cyanamide. In smaller quantities, it is used for producing light and for artificial ripening of green fruits.

**Calcium Cyanamide, $CaNCN$,** is obtained, in admixture with carbon, in the form of dark grey mass, when $CaC_2$ mixed with a little $CaCl_2$, is heated in an electric furnace at 1200°C in an atmosphere of $N_2$ gas. The dark grey mixture of calcium cyanamide and carbon is commercially sold under the name *nitrolim* for use as a fertilizer. In the soil, calcium cyanamide is hydrolysed to urea and ammonium salts :

$$CaNCN+H_2O+CO_2=CaCO_3+NH_2CN ;$$

$$NH_2CN+H_2O=CO(NH_2)_2 ; CO(NH_2)_2+2H_2O=(NH_4)_2CO_3.$$

[The manufacture of calcium cyanamide from $CaC_2$ and atmospheric nitrogen, constitutes a process of *fixation of atmospheric nitrogen*, and through such process, some of atmospheric nitrogen are introduced into the plant kingdom.] When heated with steam under pressure, calcium cyanamide forms ammonia : $CaNCN+3H_2O=2NH_3+CaCO_3$. When leached with cold acidified water, calcium cyanamide forms dicyandiamide : $2CaNCN+4H_2O=2Ca(OH)_2+(NH_2CN)_2$.

Calcium cyanamide is used to manufacture fertilizers and also chemicals of the guanidine group.

**Calcium Phosphate, $Ca_3(PO_4)_2$,** occurs naturally as minerals *phosphorite* and *apatite*. It is also a major constituent of animal bones. It is formed as a voluminous flocculent white precipitate on adding a solution of disodium hydrogen phosphate to an ammoniacal solution of a calcium salt : $3CaCl_2+2NH_4OH+2Na_2HPO_4=Ca_3(PO_4)_2+4NaCl+2NH_4Cl+2H_2O$. Calcium phosphate is sparingly soluble in water, but it readily dissolves in dilute minaral acids and in an aqueous solution of phosphoric acid. In the latter case, calcium monophosphate or calcium dihydrogen phosphate is formed, which is the principal ingredient of the fertilizer called **superphosphate of lime** : $Ca_3(PO_4)_2+4H_3PO_4=3Ca(H_2PO_4)_2$.

[When powdered phosphorite mineral is digested with sulphuric acid, the 'triple phosphate' of commerce is obtained. The product is actually impure calcium dihydrogen phosphate. It is used as a fertilizer.]

**Manufacture of Superphosphate of Lime :** Superphosphate of lime is a very useful fertilizer. It is actually a mixture of monocalcium phosphate, $Ca(H_2PO_4)_2$, and calcium sulphate dihydrate, $CaSO_4.2H_2O$, containing small amounts of dicalcium phosphate, $CaHPO_4$ or $Ca_2(HPO_4)_2$. Superphosphate of lime is generally manufactured by treating powdered *apatite* or *phosphorite rock* with 70% $H_2SO_4$ (generally, the Lead Chamber acid is used) ;

$$Ca_3(PO_4)_2+2H_2SO_4+4H_2O=Ca(H_2PO_4)_2+2(CaSO_4.2H_2O).$$

Finely powdered apatite or phosphorite rock is intimately mixed with about its weight of $H_2SO_4$ in cast-iron vats fitted with mechanical stirrers. The moist mass is then kept in a closed pit (called '*superphosphate den*'), provided with a vent pipe for the escape of waste gases, for about 10-12 hours, when the reaction is complete. The product is then stored for maturation over a period of about 3 months. The dry mass is then sold in the market as **'superphosphate of lime'.**

**Tests for calcium** : (i) Calcium salts give a brick-red colour in the **flame test.** (ii) When ammonium oxalate soln. is added to a soln. of a calcium salt, a white crystalline precipitate of calcium oxalate, soluble in mineral acids, but insoluble in acetic acid, is obtained. (iii) On adding ammonium carbonate soln. to a neutral or ammoniacal soln. of a calcium salt, a white precipitate of $CaCO_3$, soluble in acetic acid (and also in mineral acids) is formed.

Quantitative estimation of calcium is done by precipitating it from a soln. as calcium oxalate and igniting the ppt. to CaO and weighing. *Alternatively*, the ppt. of calcium oxalate may be dissolved in dil. $H_2SO_4$ and the liberated oxalic acid titrated with standard $KMnO_4$ solution.

## STRONTIUM

*Symbol* : Sr ; *Atomic No.*=38 ; *Atomic wt.*=87·63

*Electronic configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2$

**OCCURRENCE** : Strontium does not occur abundantly in nature. Besides its two principal ores, **Strontianite ($SrCO_3$)** and **Celestine** ($SrSO_4$), the metal is generally associated in small quantities with the minerals of the other alkaline earth metals. India possesses only some small amounts of the sulphate ore at Tamilnadu.

**EXTRACTION** : Strontium is generally extracted by the electrolysis of fused strontium chloride or by the reduction of strontium oxide by thermit process. For the electrolytic process, strontium chloride is prepared by dissolving powdered strontianite ore in HCl. Chlorine gas is passed through the solution to oxidise ferrous chloride to the ferric state, and the solution is boiled with a little $Na_2CO_3$ to precipitate iron as ferric hydroxide. From the filtered solution, strontium chloride is crystallised. Anhydrous strontium chloride is fused with a little KCl, and the melt is electrolysed in an exactly analogous method used for the electrolytic extraction of calcium. In the **Thermit process,** strontium oxide is obtained either from strontianite or celestine. Strontianite ($SrCO_3$) is either thermally decomposed to SrO and $CO_2$, or it is decomposed by superheated steam to $Sr(OH)_2$, which is subsequently ignited at about 700°C to the oxide : $SrCO_3+H_2O=Sr(OH)_2+CO_2\uparrow$ ; $Sr(OH)_2=SrO+H_2O$. When celestine is used as the source, the ore is reduced by heating with coke to strontium sulphide, which is then boiled with strong alkali solution to produce $Sr(OH)_2$. The hydroxide is ultimately ignited to the oxide : $SrSO_4+4C=SrS+4CO\uparrow$ ; $SrS+2NaOH=Sr(OH)_2+Na_2S$ ; $Sr(OH)_2=SrO+H_2O$.

In the actual reduction, SrO is mixed with aluminium powder and the mixture is ignited. At the high temperature attained, aluminium reduces SrO to metallic strontium which is volatilised above 950°C and is condensed in a cooled receiver : $3SrO+2Al=Al_2O_3+3Sr$.

**PROPERTIES :** Strontium is a bright silver-white metal (mp. 800°C, b.p. 1366°C, sp. gr. 2.54). It is malleable and ductile. It is softer than calcium, but is more reactive than it. It is hardly acted upon by dry air, but on exposure to moist air, it tarnishes by forming a thin film of the oxide on its surface. It burns vigorously in air when heated and forms the oxide and the nitride. At ordinary temperatures, it docomposes water to form hydrogen. The metal reacts vigorously with acids, but it has no action on alkalis. It directly combines on heating with chlorine, sulphur and nitrogen to form the corresponding binary compounds, and as such, resembles calcium closely. It is a good reducing agent.

**USES :** The metal has some use in certain photocells. The salts of the metal are used in colour pyrotechnics.

**COMPOUNDS OF STRONTIUM :** As is expected, strontium forms salts which closely resemble those of calcium, and in all of them, the metal exhibits a valency of +2 units.

**Strontium Hydride, $SrH_2$,** is obtained by heating the metal-amalgam in a stream of hydrogen, and it resembles $CaH_2$ in both appearance and properties, although it is a little more stable than $CaH_2$.

**Strontium Oxide and Hydroxide, SrO and $Sr(OH)_2$ :** Strontium oxide or strontia (SrO) is generally prepared, like CaO, by the thermal decomposition of the carbonate at a much higher temperature than that needed for the production of CaO. (This is due to the fact that the dissociation pressure of $SrCO_3$ is smaller than that of $CaCO_3$.)

Industrially, SrO is prepared from strontianite or celestine ores, as described in the extraction of the strontium by the thermit process. It is an amorphous white solid (sp. gr. 3.95—4.6), but can also be obtained in a crystalline form. Amorphous SrO absorbs $CO_2$ from air and combines with water with vigorous evolution of heat (*slaking*), first forming the hydroxide, $Sr(OH)_2$. With excess of water, an octahydrate $Sr(OH)_2.8H_2O$, is formed which, on controlled heating, may be degraded to the monohydrate, $Sr(OH)_2.H_2O$.

Strontium hydroxide is obtained by slaking SrO, or by the action of superheated steam on strontium carbonate. It is a colourless crystalline solid, more soluble in water and is a stronger base than $Ca(OH)_2$. On heating at 100°C, it loses a molecule of water to form SrO. It forms an insoluble precipitate of strontium saccharate, $2SrO.C_{12}H_{22}O_{11}$, with a solution of cane sugar and the reaction is often used in sugar industry for de-sugaring molasses. Calcium saccharate deposits $SrCO_3$ and releases sugar on treatment with $CO_2$.

**Strontium Peroxide, $SrO_2.8H_2O$,** is obtained as a white powder by the action of $H_2O_2$ or $Na_2O_2$ on a solution of strontium salt. It is sparingly soluble in water and is decomposed by acids to $H_2O_2$. The anhydrous peroxide may be obtained by gentle heating (100-130°C) of the hydrated variety. On stronger heating, the anhydrous compound decomposed into SrO and oxygen.

**Strontium Chloride, $SrCl_2$,** is most simply prepared by dissolving the carbonate in hydrochloric acid and crystallising below 60°C, when the hexahydrate, $SrCl_2.6H_2O$ is obtained. It forms deliquescent hexagonal needles, isomorphous with $CaCl_2.6H_2O$. Above 60°C, the dihydrate, $SrCl_2.2H_2O$, crystallises in rectangular plates. On heating the hydrated salts above 100°C, the anhydrous salt may be obtained, which melts at 872°C. It is highly soluble in water, and the solution has a sharp bitter taste. Unlike $CaCl_2$. $6H_2O$, the strontium salt is sparingly soluble in ethyl alcohol ; but, it reacts with ammonia to form the addition product, $SrCl_2$. $8NH_3$, like the calcium salt.

Srontium Bromide and Strontium Iodide can be prepared by methods similar to those for preparing the corresponding calcium salts. They have melting points of 643°C and 507°C respectively. They are readily soluble in alcohol, and resembles the corresponding calcium salts in their properties.

**Strontium Carbonate, $SrCO_3$,** occurs in nature as *Strontianite*. Pure $SrCO_3$ is obtained by precipitating it from an aqueous solution of a strontium salt with $(NH_4)_2CO_3$ solution. It is industrially prepared by fusing a mixture of powdered celestine ore and sodium carbonate. The cooled melt is leached with water to dissolve out sodium sulphate, and $SrCO_3$ is left as a white residue : $SrSO_4+Na_2CO_3=SrCO_3+Na_2SO_4$. It is a white substance, sparingly soluble in water. The aqueous solution has a basic reaction due to partial hydrolysis. The presence of dissolved $CO_2$ in water raises the solubility of $SrCO_3$ considerably. The solid occurs in two forms—rhombic and hexagonal,—the former changing to the latter at 929°C.

**Strontium Nitrate, $Sr(NO_3)_2$,** may be obtained by dissolving the carbonate in $HNO_3$, or by the double decomposition between $SrCl_2$ and $NaNO_3$ solutions.

$$SrCO_3+2HNO_3=Sr(NO_3)_2+CO_2+H_2O\ ;$$
$$SrCl_2+2NaNO_3=Sr(NO_3)_2+2NaCl.$$

It is a colourless crystalline solid (m.p. 645°C, sp. gr. 2.93), highly soluble in water (100 gms. water dissolve 70.8 gms. of the salt at 20°C).

The salt is generally obtained as the tetrahydrate, $Sr(NO_3)_2 . 4H_2O$, in the monoclinic form, but it can be made anhydrous by heating at 100°C. On heating, it first loses oxygen to form the nitrite, $Sr(NO_2)_2$, but at higher temperatures, SrO is formed. It is used in pyrotechnics.

**Strontium Sulphate, $SrSO_4$,** occurs in nature as *celestine*, which is the starting material for the technical preparation of the metal and most of its salts. In the laboratory, it may be prepared by adding a solution of $Na_2SO_4$ to a solution of $SrCl_2$ in water and then filtering off the precipitated $SrSO_4$ : $SrCl_2+Na_2SO_4=SrSO_4+2NaCl$. It is a colourless solid (sp. gr. 3.9-4) and is less soluble in water than $CaSO_4$. Unlike $CaSO_4$, it is insoluble in a strong solution of ammonium sulphate as well. But, it dissolves in conc. $H_2SO_4$ to form a double salt, $SrSO_4.H_2SO_4$. It also forms many sparingly soluble double salts with alkali metal sulphates and ammonium sulphate. It melts on strong heating (white-heat) with simultaneous decomposition, losing $SO_3$. :

$$SrSO_4=SrO+SO_3.$$

Tests : (i) Strontium salts impart characteristic *crimson* colour to the non-luminous Bunsen flame (Flame Test). Quantitatively, Sr may be estimated either gravimetrically by weighing as dried $SrSO_4$, or volumetrically, by titrating the precipitate of strontium oxalate dissolved in dil. $H_2SO_4$, with standard $KMnO_4$ solution.

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## BARIUM

*Symbol* : Ba ; *Atomic No.*=56 ; *Atomic wt.*=137·36.

*Electronic configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2$.

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OCCURRENCE : The principal ores of barium are : (i) **Barytes or Heavy Spar, ($BaSO_4$)** and (ii) **Witherite ($BaCO_3$)**. Somewhat less important ores are : (iii) **Alstonite** or **Baryto-calcite ($BaCO_3.CaCO_3$)** and the spinel, **Psilomelane** ($BaO.MnO_2$). Barium sulphate is associated with many minerals of lead.

EXTRACTION : As in the case of strontium, the extraction of barium is also done by the electrolytic process and the thermit process. In the electrolytic process, a hot solution of barium chloride is electrolysed in a cell using mercury cathode. Barium is liberated at the cathode and forms an amalgam, which is heated in vacuum at 1200°C, when mercury distils over, leaving behind almost pure metallic barium.

[Barium chloride, used as the electrolyte, is obtained by dissolving *Witherite* in HCl and crystallising the salt.]

In the **thermit process,** a mixture of powdered barium oxide and aluminium powder is mixed with about 10% barium peroxide and the mixture is heated in an iron tube at 1200°C. Barium oxide is reduced to the metallic state and the vapours of the metal are condensed in a cooled steel receptacle : $3BaO+2Al=Al_2O_3+3Ba$.

[The reduction may also be carried out by heating with silicon or calcium at somewhat elevated temperatures (1900°—2000°C).]

For preparing the starting material (BaO) of the Thermit process, the mineral heavy spar ($BaSO_4$) is generally used. It is reduced by heating with carbon to barium sulphide, which is hydrolysed by superheated steam to barium hydroxide. Barium hydroxide is dehydrated to BaO by heating : $BaSO_4+4C=BaS+4CO$ ; $BaS+2H_2O=Ba(OH)_2+H_2S\uparrow$ ; $Ba(OH)_2\xrightarrow{\text{heat}}BaO+H_2O$.

On a very small scale, pure barium metal is most readily obtained by the thermal decomposition of barium azide, $Ba(N_3)_2$ : $Ba(N_3)_2\longrightarrow Ba+3N_2\uparrow$ .

**PROPERTIES :** Barium is a bright silver-white, soft but heavy metal (m.p. 710°C, b.p. 1537°C, sp. gr. 3.78). It is malleable and ductile, and is a good conductor of heat and electricity. Barium resembles other alkaline earth metals in its chemical properties, but it is more reactive than its congeners, *viz*. Sr and Ca. Finely powdered barium bursts into flame in contact with air and forms the oxide. When heated in air, it forms mainly BaO, together with a little $BaO_2$. It readily reacts with water and alcohol at ordinary temperatures and sets free hydrogen. It unites directly, when heated, with oxygen, nitrogen, sulphur, halogens and hydrogen to form the corresponding binary compounds. The metal forms amalgam with mercury and alloys with many other metals. It is a good reducing agent.

**USES :** Alloys of barium with magnesium, aluminium and lead are used for making some machine-parts. The metal is used for removing gases from valves and vacuum tubes.

## COMPOUNDS OF BARIUM.

**Barium Hydride, $BaH_2$,** is formed as a colourless crystalline solid, on heating the metal or its amalgam in a current of dry hydrogen at about 1400°C. It is a salt-like hydride, but is the least stable among the hydrides of alkaline earth metals. It is decomposed by water to form barium hydroxide and hydrogen.

**Barium Oxide and Hydroxide, BaO and $Ba(OH)_2$ :** Barium oxide or *baryta* is best obtained in the pure state by strongly igniting barium nitrate : $2Ba(NO_3)_2=2BaO+4NO_2\uparrow+O_2\uparrow$ . It is generally prepared on the large scale by the thermal decomposition of barium carbonate (mixed with carbon) : $BaCO_3+C=BaO+2CO\uparrow$ . (The purpose of using carbon is to remove $CO_2$ by converting it to CO, so that, inspite of the low $CO_2$-pressure, the decomposition of $BaCO_3$ proceeds to completion.) Barium oxide is a white infusible powder (sp. gr. 4.7-5.8). It reacts with water (*slakes*) with the evolution of much heat, forming barium hydroxide : $BaO+H_2O=Ba(OH)_2+22.25$ kcals. It is more soluble in water than CaO or SrO. Barium oxide is a strongly basic oxide and absorbs moisture and $CO_2$ from air. When heated at about 500°C in air or oxygen, barium oxide is transformed into barium peroxide ; but, at higher temperatures, the resultant peroxide is decomposed into barium oxide and oxygen : $2BaO+O_2\rightleftharpoons 2BaO_2$. It is chiefly used as a desiccant and for the preparation of the hydroxide and the peroxide.

Barium hydroxide is the product of union of BaO with water, and is usually prepared by slaking BaO with water, or by the action of superheated steam on barium carbonate. The anhydrous substance is a white amorphous powder which melts (320°C.) without decomposition. On further heating, it is converted to BaO. It is considerably more soluble in water than the hydroxides of the other alkaline earth metals, and the solution is generally known as *baryta-water*, which is used as a standard alkali for volumetric titrations. [The barium hydroxide solution readily reacts with atmospheric $CO_2$ to form insoluble $BaCO_3$, and as such, the standard solution of $Ba(OH)_2$ should be kept out of contact with air.] Hydrated barium hydroxide, $Ba(OH)_2.8H_2O$, crystallises out, when the solution of barium hydroxide is concentrated. Solid $Ba(OH)_2$ is largely thrown out of its solution on adding alcohol. It forms insoluble barium saccharate with sugar solution, and is, therefore, used in sugar industry for recovery of sugar from molasses.

**Barium Peroxide, $BaO_2$,** is prepared on a large scale by heating BaO at 500°C in a current of dry and $CO_2$-free air or oxygen : $2BaO+O_2\rightleftharpoons 2BaO_2$ ($\Delta H=+24{,}000$ cals.). The reaction is reversible and the back-reaction (*i.e.* the decomposition of $BaO_2$ to BaO and $O_2$) takes place at higher temperatures (700°C). [This reaction was the basis of the presently obsolete Brin's process of manufacturing oxygen.] The hydrated peroxide, $BaO_2.8H_2O$, can be prepared by the reaction of $H_2O_2$ with a cold solution of barium hydroxide. The hydrated salt becomes anhydrous on heating at 130°C.

Barium peroxide is a white powder, sparingly soluble in water and insoluble in alcohol and ether. The anhydrous salt absorbs water to form the octahydrate, $BaO_2.8H_2O$. The aqueous suspension of barium peroxide acts as an oxidant for ferrous salts, but as a reducing agent for potassium ferricyanide : $BaO_2+2K_3[Fe(CN)_6]=K_6Ba[Fe(CN)_6]_2+O_2$. It also reduces mercuric chloride to metallic mercury : $BaO_2+HgCl_2=Hg+BaCl_2+O_2$. Dilute acids liberate hydrogen peroxide from $BaO_2$, which is supposed to be the salt the of very weak acid, $H_2O_2$, so that it is displaced from its salt by stronger acids : $BaO_2 + 2H^+ = Ba^{++} + H_2O_2$.

Barium peroxide is used in bleaching silk, vegetable fibres and straw. It is used for the manufacture of hydrogen peroxide, barium peroxycarbonate *etc.* It has also some application for decolorizing lead glass and as a disinfectant. It is also used as the igniter in thermit process.

**Barium Chloride, $BaCl_2.2H_2O$,** may be prepared by the action of dil. HCl on powdered barium carbonate (or *Witherite* mineral). The resultant solution gives $BaCl_2.2H_2O$ crystals on concentration. It is also prepared from *heavy spar* by strongly heating the powdered ore with carbon and calcium chloride (by-product from Solvay Process). The carbon reduces barium sulphate to barium sulphide, and this reacts with calcium chloride to form barium chloride and calcium sulphide. $BaSO_4 + 4C = BaS + 4CO$ ; $BaS + CaCl_2 = BaCl_2 + CaS$. Barium chloride is leached from the cooled mass by hot water. Any calcium sulphide, remaining in solution, is precipitated by adding lime, when insoluble CaO.CaS is precipitated. This is filtered and the filtrate is evaporated to crystallisation.

Hydrated barium chloride is a colourless crystalline solid, soluble in water, but insoluble in alcohol and in conc. HCl. It becomes anhydrous on heating. The anhydrous substance (sp. gr. 3.86) melts at 878°C. The substance is poisonous.

Barium chloride is industrially used to soften boiler feed-water containing gypsum, and for the preparation of other barium compounds. It is used in photography and medicine, and also as a laboratory reagent for the detection and estimation of sulphate.

**Barium Fluoride ($BaF_2$) :** Barium fluoride is obtained as a white precipitate on adding potassium fluoride solution to an aqueous solution of barium chloride :

$$BaCl_2 + 2KF = BaF_2 \downarrow + 2KCl.$$

The precipitate is filtered, washed with water and dried in air.

**Barium Bromide and Barium Iodide, $BrBr_2$ and $BaI_2$,** are readily prepared by the reactions between $Ba(OH)_2$ or $BaCO_3$ and HBr or HI. They are white substances, readily soluble in water and alcohol. Both these salts form dihydrates which can be made anhydrous by heating.

**Barium Chlorate [$Ba(ClO_3)_2$] :** On passing chlorine gas at 180°C through a solution of barium hydroxide, barium chlorate is formed. It is isolated as white crystals by the fractional crystallisation of the reaction-mixture : $6Ba(OH)_2 + 6Cl_2 = Ba(ClO_3)_2 + 5BaCl_2 + 6H_2O$. It is used in preparing fireworks and also for the production of chloric acid.

**Barium Carbonate, $BaCO_3$,** occurs in nature as *Witherite.* It may be prepared by the double decomposition between aqueous solutions of barium chloride and sodium carbonate, or by passing $CO_2$ through baryta-water. It is a white amorphous substance, sparingly soluble in water, but it dissolves in acids with the evolution of $CO_2$. Barium carbonate loses $CO_2$ at considerably higher temperatures than the carbonates of other alkaline earth metals ($>1400°C$).

Barium carbonate is used for the production of easily fusible, heavy glasses of high refractive index. It is also used in ceramic industries, as well as for the preparation of other barium compounds. It is used in paints.

**Barium Nitrate, $Ba(NO_3)_2$,** is prepared by dissolving the oxide, the hydroxide or the carbonate of the metal in dil. $HNO_3$ and crystallising the salt by evaporation of the solution. On a large scale, it is prepared by the double decomposition between barium chloride and sodium nitrate (Chile saltpetre), or barium carbonate and calcium nitrate. At ordinary temperatures, barium nitrate crystallises as anhydrous colourless crystals, moderately soluble in water (solubility at 20°C is 9.2 gms.). It melts at 575°C and has a density of 3.24. When it is strongly heated, oxygen is first evolved, forming barium nitrite, which decomposes to the oxide on further heating : $Ba(NO_3)_2 = Ba(NO_2)_2 + O_2$ ; $2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2$. Barium nitrate is used for preparing pure BaO and $BaO_2$ and also for the production of explosives and pyrotechnics (green colour).

**Barium Sulphide, BaS,** is industrially prepared through the reduction of barytes ($BaSO_4$) with carbon by strong heating in a rotary kiln : $BaSO_4 + 4C = BaS + 4CO \uparrow$. It is also manufactured by the action of carbon disulphide vapour on barium carbonate (powdered *witherite* ore) : $2BaCO_3 + CS_2 = 2BaS + 3CO_2 \uparrow$.

It is a white substance, slightly soluble in water, undergoing hydrolysis thereby : $2BaS + 2H_2O = Ba(SH)_2 + Ba(OH)_2$ ; $Ba(SH)_2 + 2H_2O = Ba(OH)_2 + 2H_2S$. It has phosphorescent properties. It is used as insecticide and for the production of lithopone and luminous paints.

**Barium Sulphate, $BaSO_4$,** is widely distributed in nature as the ore of barium, *viz.* **barytes** or **heavy spar.** It is often found in well-formed colourless rhombic crystals of density 4-4.8. It may be prepared in the laboratory as a white heavy precipitate, by adding sulphuric acid or a soluble sulphate to a solution of barium salts or baryta-water. The product forms fine white precipitate, sparingly soluble in water and dilute acids, but it dissolves in conc. $H_2SO_4$ due to the formation of soluble $Ba(HSO_4)_2$. It is insoluble in concentrated ammonium sulphate solution (distinction from $CaSO_4$). Barium sulphate is notable for its extreme stability against heat ; it is unaffected even at

1500°C. For its insolubility and stability against heat, it is used in the detection and estimation of sulphate or sulphuric acid. Barium sulphate is reduced to BaS on strongly heating with coke : $BaSO_4+4C=BaS+4CO$.

Barium sulphate is widely used as a filler for paper, especially for wall-papers, cartons, coloured papers and photographic papers, on which it confers excellent glaze. It is also used in rubber, leather and ceramic industries. It is used as pigment, but as its covering power is rather poor, it is used in admixture with zinc sulphide, under the name **Lithopone.** [Lithopone is manufactured through the interaction of BaS and $ZnSO_4$, and heating the resultant precipitate at 50°—60°C : $BaS+ZnSO_4=\underbrace{BaSO_4+ZnS}_{\text{(Lithopone)}}$.]

Because of the high absorption of X-rays by $BaSO_4$, it is used to render visible the contours of the stomach and intenstinal tract in radiological examinations. (Its excessive insolubility makes its quite non-poisonous.)

**Barium Chromate, $BaCrO_4$,** is obtained as a yellow precipitate, on adding a solution of alkali chromate or dichromate to a solution of a barium salt. It is sparingly soluble in water and acetic acid, but is readily soluble in dilute mineral acids.

**Tests for Barium :** (i) Barium salts give a characteristic apple-green persistent flame in the flame test. (ii) A solution of barium salt gives a white precipitate of $BaSO_4$ with $H_2SO_4$ or a soluble sulphate soln. The precipitate is insoluble in acids and ammonia. (iii) A solution of barium salt gives a yellow ppt. of $BaCrO_4$ on treatment with an alkali chromate or dichromate soln. The ppt. is insoluble in acetic acid, but soluble in mineral acids (except $H_2SO_4$).

Gravimetrically, barium is estimated by precipitating as $BaSO_4$ or $BaCrO_4$ and drying the ppt. at 110°C. The ppt. of $BaCrO_4$ may also be dissolved in dil. mineral acid, KI added and the liberated iodine may be titrated with standard sodium thiosulphate solution to ascertain the amount of barium.

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## RADIUM

*Symbol* : Ra ; *Atomic No.*=88 ; *Atomic wt.*=226·05

*Electronic Configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}$
$5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2$

---

**Occurrence** : Radium is invariably associated with uranium minerals, where it is formed as a disintegration product. **Pitchblende or Uraninite** ($U_3O_8$) is the richest source of radium, where it is present to the extent of $2 \times 10^{-5}$ per cent. Another rich mineral is **Carnotite,** $K_2O.\ 2UO_3.\ V_2O_5.\ 3H_2O$. The less important ores are **Autunite** $[Ca(UO_2)_2(PO_4)_2]$ and **Monazite sand.**

Monazite sand is abundantly available in India (Travancore area) and small quantities of pitchblende have also been found in some parts of this country.

Radium was discovered (1898) by Pierre Curie and Madam Curie in conjunction with Bemont. The discovery followed from the observation that certain uranium minerals like *pitchblende* possessed higher radioactivity than that corresponding to their uranium-content, and as such, they must have contained radioactive materials other than uranium. In search of such new radioactive materials, the Curies first disocvered polonium and then radium. The metal was isolated in 1910 by Mme. Curie and Debierne.

**Extraction :** Radium is obtained by the electrolysis of radium halide (mainly, chloride) in aqueous solutions with mercury cathode and platinum-iridium alloy anode. Radium amalgam formed is subsequently heated in a current of hydrogen under reduced pressure at 700°C, when mercury distils over, leaving bright white pure radium.

Radium halides used in the electrolysis are mainly obtained from pitchblende or carnotite. When *pitchblende* is used, the finely divided ore is roasted and is then leached with $H_2SO_4$. Barium chloride solution is added to this extract. Barium sulphate is precipitated, with which radium sulphate is co-precipitated. Silver and lead, contained in the ore, are also precipitated simultaneously. Silver is removed by treatment of the precipitate with sodium thiosulphate solution, and lead by boiling the precipitate with caustic soda solution. The residue is then boiled with sodium carbonate solution to convert the sulphates of Ba and Ra into their carbonates. These are dissolved in HCl, and the resulting mixture of $BaCl_2$ and $RaCl_2$ is submitted to repeated fractional crystallisation (the less soluble $RaCl_2$ separates out first). After much of the barium has been removed in this way, the chlorides are converted to bromides, and these in turn are submitted to systematic fractional crystallisation, until the desired degree of purity is reached.

When *carnotite* is used, the finely divided ore is roasted at 700°C and then digested with hot soda solution, when uranium and vanadium go into solution as uranate and vanadate. The residue (containing all the radium) is boiled with $HNO_3$ and filtered. The filtrate is mixed with uranate and vanadate solution obtained earlier and the residue is rejected. The mixed solution is treated with $Na_2CO_3$ solution, when radium carbonate, along with barium carbonate, is precipitated. The precipitate is digested with $H_2SO_4$, when a mixture of barium sulphate and radium sulphate is obtained. This is converted into chloride or bromide and then fractionally crystallised to get radium halides.

**Properties :** Radium is a brilliant white metal (m.p. 700°C) which decomposes cold water and rapidly tarnishes in air due to the formation of oxide and nitride. Chemically, it closely resembles barium, but is more volatile. Its salts give red flame-coloration. Radium is radioactive and emits $\alpha$-rays. Its half life period is 1590 years.

**Compounds of radium :** As would be expected, they resemble barium compounds very closely (but are usually less soluble) and are similarly prepared. The following compounds of radium are known : $Ra(OH)_2$, $RaCl_2. 2H_2O$, $RaBr_2.2H_2O$, $RaSO_4$. $Ra(NO_3)_2$, $Ra_3N_2$ *etc.*

**Uses :** Owing to the rarity and very high cost, radium or its salts have found few uses. The chief use is in medicine as a localised source of radioactive rays for the treatment of malignant tumors (cancer). Small amounts of radium salts are also used in the manufacture of luminous paints (*e.g.* for watch-dials, push-buttons, street signs *etc.*) These are essentially zinc sulphide, with a minute trace of radium to excite fluorescence.

## ELEMENTS OF THE SUB-GROUP IIB

### ZINC

*Symbol* : Zn ; *Atomic No.*=30 ; *Atomic weight*=65·38.
*Electronic Configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$.

**Occurrence :** Zinc does not occur free in nature. The ores of zinc are rather widely distributed. The principle ores are :

(i) The sulphide, **Zinc blende, Sphalerite** or **'Black jack'** (ZnS), (ii) the carbonate, **Calamine** or **Smithsonite** ($ZnCO_3$), (iii) the silicates, **Electric Calamine** ($Zn_2SiO_4.H_2O$), (iv) the oxide, **Zincite** or **Red zinc ore** (**ZnO**, very rare ore), and (v) **Franklinite** ($ZnO.Fe_2O_3$).

**Indian source :** In India, zinc is available as zinc blende in the mines near Udaipur (Rajasthan).

**Extraction :** For the extraction of zinc, usually zinc blende is used as the ore. Calamine is also used in certain cases. Two processes are generally used for the extraction of zinc. These are : (i) the carbon-reduction process and (ii) the electrolytic process.

### (i) CARBON-REDUCTION PROCESS.

(a) *Concentration of the ore* : Finely powdered zinc blende is agitated (by a stream of air) with water, containing eucalyptus or pine oil and a small quantity of acid, in a large reservoir. Galena (PbS), which occurs with zinc blende, collects as scum on the surface of the liquid and is removed. The second agitation after addition of a little more oil and acid, produces froth which contains most of the zinc blende, while the gangue materials sink to the bottom. The froth or scum is collected, dried and is used in the subsequent operations.

(b) *Roasting* : The 'concentrated' ore is then heated in multiple-hearth furnace provided with mechanical stirrer, while air is allowed to flow over heated ores. All of the sulphide must be completely oxidised to the oxide. If some of it is converted to zinc sulphate ($ZnS+2O_2=ZnSO_4$), this sulphate is again converted to zinc sulphide in the subsequent reduction process (smelting) and the zinc metal, finally obtained, contains zinc sulphide as an impurity. [High temperature is used in the roasting process in order to ensure that, even if some zinc sulphate is formed earlier, it is decomposed to zinc oxide.] If calamine ore is used, it is also transformed into ZnO during roasting.

$$2ZnS+3O_2=2ZnO+2SO_2\ ;\ ZnCO_3=ZnO+CO_2.$$

$$2ZnSO_4=2ZnO+2SO_2+O_2.$$

[The sulphur dioxide formed during the process may be used for the manufacture of $H_2SO_4$.]

(c) *Reduction* (Smelting) : The roasted ore is mixed with about one-fourth of its weight of powdered anthracite coke and charged into retorts (A) made of fire-bricks and set in rows in slightly inclined position (one above another) in a gas-fired furnace. The retorts are charged first and then their open ends are fitted with earthen-ware condensers (B), carrying iron prolongs (C). [fig. 13.7]. These are then heated (generally by producer gas) to nearly 1400°C, when zinc oxide is reduced by carbon, forming zinc metal and carbon monoxide : $ZnO+C=Zn+CO$. [Excess coke is used in the mixture to prevent the formation of $CO_2$, which tends to oxidise zinc powder to zinc oxide : $Zn+CO_2=ZnO+CO$].

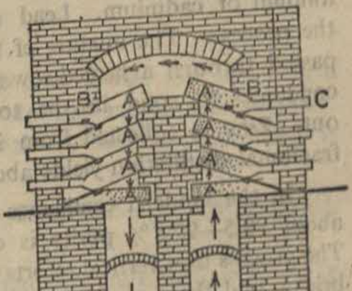


Fig. 13.7

Carbon monoxide (together with a little zinc-vapour) burns at the mouth of the prolongs with bluish flame. When the reduction of ZnO is completed, the temperature of the furnace increases, the bluish flame dies and some zinc-vapour burns at the mouth of the prolongs with dazzling white flame. This indicates the completion of the heating operation. So, the supply of fuel gas is cut off at this point and the furnace is allowed to cool down. During the process, zinc vapour distils over and most of it is collected in the condensers as a liquid. The rest is collected as zinc dust in the prolongs. The molten metal is collected from time to time and allowed to solidity into impure zinc ingots, called the **spelter.**

(d) *Refining* : Zinc metal of 97-98% purity is obtained by this method. The main impurities being lead, arsenic, cadmium, silicon, and carbon. The ingots of impure zinc (*spelter*) is melted by heating and the liquid melt is allowed to stand for some time, when the heavy metals (like lead, iron *etc.*) settle at the lower layer and more pure zinc remains in the upper layer. The upper layer of the molten mass is separated and zinc is purified by repeated distillation at reduced pressure after adding a small quantity of of $KNO_3$.

Refining of spelter may also be done by electrolysis. In this process, pieces of spelter are made anode and a thin zinc strip is made cathode in an electrolyte of zinc sulphate solution, acidified with $H_2SO_4$. During the electrolysis, very pure zinc is deposited at the cathode.

Refining of impure zinc may also be effected by the fractional distillation of spelter. When spelter is heated at 900°—1000°C, arsenic first distils over and then zinc distils over along with a little amount of cadmium. Lead and iron remains as residue during the process. The mixture of the vapours of zinc and cadmium is passed through a heated tower, maintained at 800°C. Zinc vapour condenses to solid in the tower, while cadmium vapour escapes out. Zinc is collected from inside the tower. A number of such fractional distillation yields about 100% pure zinc.

In the modern **continuous process** (*New Jersey process*), zinc of about 99.5—99.8% purity is directly obtained much economically. The process uses vertical retorts made of carborundum (silicon carbide) bricks, and these are heated externally at 1200° – 1300°C by burning producer gas. The charge of finely ground roasted zinc blende and coke, made into briquettes with suitable binder, is fed through the top of the retorts. As a result of the reduction of zinc oxide (roasted ore) by coke, metallic zinc and carbon monoxide are formed. Zinc is vaporised at the temperature of the retorts, and the mixture of zinc vapour and carbon monoxide passes up the retorts and escape through an outlet near the top. Producer gas is often forced into the retorts from below to drive out the zinc vapour. Carbon monoxide and zinc vapour pass through condensers, where zinc condenses to liquid and is run off into a resorvoir, and carbon monoxide escapes (Fig. 13.8). The residual ashes descend down and are removed at the base of the furnace. Zinc. thus collected, is refined by vaporising at 1100°C and fractionating the vapour in long rectifying column. Zinc, rich in cadmium, passes into the upper end of the column, fine zinc (99.995% pure) collects at the middle and small amount of zinc, with impurities like lead, copper and iron (of the original ore), is left at the bottom.

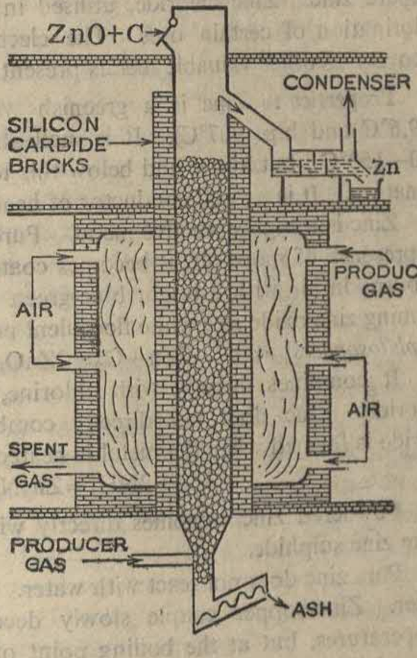


Fig. 13.8

### (II) THE ELECTROLYTIC PROCESS :

In this process, the concentrated zinc blende is roasted in a limited supply of air to give the maximum amount of zinc sulphate. The mixture of the zinc sulphate and zinc oxide, thus produced, is leached with dil. $H_2SO_4$ :

$ZnS+2O_2=ZnSO_4$ ; $2ZnS+3O_2=2ZnO+2SO_2$ ; $ZnO+H_2SO_4=ZnSO_4+H_2O$.

The resultant solution is then treated with milk of lime to make it just alkaline in order to precipitate iron, aluminium *etc.* as their hydrated oxides. This is filtered and the filtrate is agitated with zinc dust to precipitate copper and cadmium from solution, which are removed by filtration. The filtered liquor (containing mainly $ZnSO_4$) is acidified with a little $H_2SO_4$ and electrolysed with lead anodes and aluminium cathodes at a high current density (at 35°C). The zinc produced at the cathode is more than 99.9% pure.

The electrolytic process has much utility at the present times, as both low grade and siliceous ores can be worked up by it. Electrolysis of fused mixture of $ZnCl_2$ and KCl has been used occasionally to prepare zinc. Zinc chloride, utilised in this process, is prepared by chlorination of certain ores. The electrolytic methods permit the recovery of other valuable metals present in the ores.

**Properties :** Zinc is a greenish white crystalline metal (m.p. 419.6°C and b.p. 907°C). It is malleable and ductile only between 100—150°C ; but above and below this temperature range, it is brittle in nature. It is a good conductor of heat and electricity.

Zinc is a highly reactive metal. Pure zinc is stable in dry air, but in presence of moist air, it becomes coated with basic zinc carbonate. It burns in air with a bright blue-green flame, when strongly heated, forming zinc oxide as a white flocculent powder, named by the ancients as *philosophers' wool* : $2Zn+O_2=2ZnO$.

It combines directly with chlorine, when heated, to give zinc chloride. Zinc does not directly combine with nitrogen, but the nitride is formed when the metal is heated in ammonia :

$$3Zn+2NH_3=Zn_3N_2+3H_2.$$

Powdered zinc combines directly with sulphur, when heated, to form zinc sulphide.

Pure zinc does not react with water. Commercial zinc reacts with water. Zinc-copper couple slowly decomposes water at ordinary temperatures, but at the boiling point of water, it reacts vigorously. The red-hot metal decomposes steam, forming zinc oxide and hydrogen : $Zn+H_2O=ZnO+H_2$. Zn readily dissolves in dilute $H_2SO_4$ and HCl, zinc sulphate and chloride being formed ; but, the action is very slow with very pure metal (see page 335). With conc. $H_2SO_4$, it reacts very slowly at ordinary temperatures, but on heating, vigorous reaction takes place, with the formation of anhydrous zinc sulphate, $SO_2$, $H_2S$ and S. The products obtained by the action of zinc on $HNO_3$ depend on the concentration of the acid and the temperature of the reaction. Very dilute $HNO_3$ yields $NH_4NO_3$, which on further heating produces $N_2O$ ; moderately conc. $HNO_3$ yields NO, while conc. $HNO_3$ gives $NO_2$ on heating :

$$4Zn+10HNO_3 = 4Zn(NO_3)_2+3H_2O+NH_4NO_3 ;$$
$$4Zn+10HNO_3 = 4Zn(NO_3)_2+5H_2O+N_2O ;$$
$$3Zn+8HNO_3 = 3Zn(NO_3)_2+4H_2O+2NO ;$$
$$Zn+4HNO_3 = Zn(NO_3)_2+2H_2O+2NO_2.$$

Zinc reacts with hot solutions of alkalis, forming soluble alkali zincates and evolving hydrogen : $Zn+2NaOH=Na_2ZnO_2+H_2$. As it occurs high in the electrochemical series, the metal precipitates lead, copper, silver, gold *etc.* from solutions of their salts :

$$CuSO_4+Zn=ZnSO_4+Cu.$$

In the molten state, zinc is completely miscible with many metals like Cu, Ag, Au, Cd, Hg, Ca, Mn, Fe, Co, Ni, Al, Sn, Sb and As.

**Uses :** Metallic zinc is used in the extraction of noble metals like silver and gold by the cyanides process, for the de-silverisation of lead in Parke's process, as anodes in electric cells and in the manufacture of alloys like brass and German silver. It is extensively used in galvanising or sherardising iron articles or plates to prevent corrosion. Zinc is also used for the manufacture of commercially important *zinc white* and for the preparation of lithographic plates. Zinc dust and granules are used in chemical laboratories as reducing agents and for the generation of hydrogen gas.

**Galvanising and Sherardizing of articles :** Iron sheets or articles are cleaned by sand-papers (or by sand-blasts) and subsequently pickled with dil.HCl. These are thoroughly washed with water to remove adhering acids and then dipped in molten zinc, containing ammonium chloride. An adherent thin coating of zinc is deposited on the iron surface. The process is called *galvanisation*. Iron articles can also be coated with zinc by heating the cleaned articles with zinc dust at about 300°–400°C in a revolving drum for several hours. The process is known as *sherardizing*. Coating of zinc by these processes offers remarkable resistance to atmospheric corrosion.

**Zinc Dust** is a mixture of zinc powder and small quantities of zinc oxide. It is deposited in the prolongs during the extraction of zinc, and can also be produced by atomising moltent zinc with a jet of high pressure air.

*Granulated zinc* is produced by pouring molten zinc in a thin stream into cold water. The small granules of the metal offers a very large surface for a given weight of zinc and hence is very reactive.

**Important alloys** of zinc are : (i) Brass, 30 to 33% Zn and 70-67% Cu ; Muntz metal, 40% Zn and 60% Cu ; German-silver, 55% Cu, 23% Zn, 22% Ni.

## COMPOUNDS OF ZINC.

Zinc is mostly present as bivalent positive ion in its compounds. The compounds are colourless unless the other components in them are coloured.

**Zinc Hydride, $ZnH_2$,** can be prepared as a white substance by the action of $LiAlH_4$ on dimethyl zinc or on an ethereal solution of zinc iodide.

$(CH_3)_2Zn+LiAlH_4=LiAl(CH_3)_2H_2+ZnH_2$ ;

$ZnI_2+2LiAlH_4=ZnH_2+2AlH_3+2LiI$.

**Zinc Oxide, (Zinc white, ZnO),** occurs in nature as red zinc ore. It is produced by heating the metal in air, or by decomposing the nitrate or the carbonate by strong heating, and condensing the vapours of the oxide :

$$2Zn+O_2=2ZnO\ ;\ ZnCO_3=ZnO+CO_2.$$

Zinc oxide is a white powder. Its colour changes to yellow on heating, but becomes white again on cooling. It is not soluble in water. ZnO is amphoteric in character and dissolves in acids to form zinc salts and in alkalis to form alkali zincates :

$$ZnO+2HCl=ZnCl_2+H_2O\ ;\ ZnO+2NaOH=Na_2ZnO_2+H_2O.$$

It is reduced to the metal on being heated with carbon :

$$ZnO+C=Zn+CO.$$

Zinc oxide is widely used as a white paint (zinc white or Chinese white). It is preferred to white lead (basic lead carbonate) as it is not blackened by $H_2S$. It is also used in the manufacture of a green pigment, **Rinmann's green,** which is a solid solution of cobalt zincate and ZnO. It also finds uses in the preparation of medicinal ointments, medicated face-creams and talcum-powders. It is used as filler in the rubber industry.

**Zinc Peroxide, $ZnO_2$,** is obtained as the hydrated compound by the action of 30% $H_2O_2$ solution on a suspension of zinc hydroxide in water, or on sodium zincate solution. The compound has not been obtained in the perfectly pure form. It is used in medicine.

**Zinc Hydroxide,** $[Zn(OH)_2]$, can be obtained as a white precipitate by the addition of a soluble hydroxide to a solution of a zinc salt :

$$ZnSO_4+2NaOH=Zn(OH)_2+Na_2SO_4.$$

Excess of alkali must be avoided, as $Zn(OH)_2$ dissolves in it, forming soluble zincate.

Zinc hydroxide is a white powder, sparingly soluble in water, but soluble in acids and alkalis, forming the zinc salts and the zincates respectively :

$Zn(OH)_2+H_2SO_4=ZnSO_4+2H_2O$ ;

$Zn(OH)_2+2NaOH=Na_2ZnO_2+2H_2O$.

Hence, $Zn(OH)_2$ is amphoteric in nature. With excess of the rather weak base ammonium hydroxide, zinc hydroxide dissolves to form the colourless complex hydroxide, $[Zn(NH_3)_4](OH)_2$. On heating, zinc hydroxide loses water and zinc oxide is formed :

$$Zn(OH)_2 = ZnO + H_2O.$$

**Zinc Chloride,** $(ZnCl_2)$, is made by dissolving the metal or its oxide, hydroxide or carbonate in strong HCl and concentrating the solution, until the crystals of the monohydrate, $ZnCl_2.H_2O$, separate. These are collected and dried. The anhydrous salt *cannot* be prepared by simply heating the crystals of the monohydrate, because hydrolysis occurs on heating, and basic salts like $Zn(OH)Cl$ and $Zn_2OCl_2$ are formed. The anhydrous salt may be prepared by heating $ZnCl_2.H_2O$ or the metal itself in a current of dry hydrogen chloride gas.

Zinc chloride is a white crystalline solid, highly deliquescent and extremely soluble in water and also in alcohol, acetone *etc.* A concentrated solution of zinc chloride dissolves zinc oxide, and the resultant solution sets to a hard glassy mass on standing. The anhydrous salt is very hygroscopic and also absorbs ammonia, forming an addition-product.

Zinc chloride finds a wide usage as a desiccating agent and acts as catalyst in many condensation reactions in organic chemistry. It is used as a dental stopping, as a flux for soldering and as a preservative for timber. It is also used in the production of *perchment paper.*

**Other zinc halides,** *viz.* zinc fluoride $(ZnF_2)$, zinc bromide $(ZnBr_2)$ and zinc iodide $(ZnI_2)$ are generally prepared by the usual action of the corresponding hydrohalic acid on the metal or its oxide, hydroxide or carbonate. The bromide and iodide are very similar to zinc chloride in their properties. Zinc fluoride is, however, sparingly soluble in water.

All the zinc halides form double salts with alkali halides.

**Zinc Nitrate,** $[Zn(NO_3)_2]$, is prepared by heating metallic zinc, ZnO, $Zn(OH)_2$ or $ZnCO_3$ in dil. $HNO_3$. On concentrating the solution to crystallisation, crystals of $Zn(NO_3)_2.6H_2O$ are obtained :

$$ZnO + 2HNO_3 = Zn(NO_3)_2 + H_2O.$$

Zinc nitrate is a colourless, crystalline solid which is highly deliquescent. It is soluble in water. On strong heating, it decomposes into zinc oxide, nitrogen dioxide and oxygen :

$$2Zn(NO_3)_2 = 2ZnO + 4NO_2 + O_2.$$

**Zinc Phosphate, $Zn_3(PO_4)_2.4H_2O$,** is formed on heating a solution of zinc sulphate with disodium hydrogen phosphate solution. It is a white substance, insoluble in water and dilute acids. On strong heating, it forms the infusible white anhydrous salt.

**Zinc Ammonium Phosphate, $Zn(NH_4)PO_4$,** is obtained as a crystalline white precipitate, by the addition of disodium (or diammonium) hydrogen phosphate to a nearly neutral (pH=6.6) solution of zinc salt in presence of $NH_4Cl$. The precipitate is soluble in ammonia and dilute acids. On heating at about 900°C, zinc ammonium phosphate is converted to zinc pyrophosphate, $Zn_2P_2O_7$.

**Zinc Sulphide, ZnS,** occurs in nature as **zinc blende** or **sphalerite.** (The naturally occuring material in generally dark in colour due to impurities like FeS.) Zinc sulphide is usually prepared by adding ammonium sulphide solution to a solution of zinc salt, or by passing $H_2S$ into a faintly acidic solution of a zinc salt. It is precipitated as a white amorphous material from the solution, and the freshly precipitated substance is readily soluble in dilute acids ; but, it gradually changes, on standing, to a less soluble form. It can also be prepared by heating the metal or its oxide with sulphur. Pure zinc sulphide does not exhibit phosphorescence ; but, the presence of impurities like copper, lead, manganese *etc.* make it phosphoresce, not only in the ordinary light, but also in the ultraviolet light and in X-rays.

Zinc sulphide is used for making phosphorescent screens for X-rays, radio-active studies and also in radar and television. [For this purpose, *Sidot's blende* is used, which is prepared by fusing ZnS with mineralizing agent.] It is also used in luminous paints (for dials of watches and clocks *etc.*) and in the white pigment, *lithopone.*

**Lithopone :** It is an equimolecular mixture of zinc sulphide and barium sulphate, and is obtained by adding barium sulphide to a solution of zinc sulphate (double decomposition) : $ZnSO_4+BaS=BaSO_4+ZnS$. The precipitate is filtered and dried by heating. The powdery white material is used as a pigment under the name *lithopone.* Lithopone is much cheaper than white lead and is non-poisonous. It is also not blackend by the action of $H_2S$ gas. But, it is much inferior to white lead or zinc white in its covering power and durability. Many varieties of lithopone turn grey on exposure to sunlight.

**Zinc Sulphate, ($ZnSO_4$),** can be prepared by the general methods of preparation of other zinc salts, *viz.* by dissolving the metal, ZnO, $Zn(OH)_2$ or $ZnCO_3$ in dil.$H_2SO_4$. The solution, on concentration and cooling, yields crystals of $ZnSO_4.7H_2O$ (*white vitriol*). It is manufactured by roasting zinc blende in a limited supply of air (below 700°C), when most of the sulphide is oxidised to the sulphate. It is then cooled, extracted with water and the filtrate is concentrated to crystallisation.

Zinc sulphate hepta-hydrate is a water-soluble, white, crystalline solid. It slowly effloresces in air at ordinary temperatures, and is converted into the anhydrous $ZnSO_4$ by heating at about 300°C. Above 300°C, it loses $SO_3$, forming oxide, ZnO : $ZnSO_4 = ZnO + SO_3$.

Zinc sulphate finds wide usage as mordant in dyeing and as a preservative in tanning industry. It is used in medicine and in the manufacture of lithopone, an useful white pigment.

**Zinc Carbonate,** ($ZnCO_3$), is found in nature as *Calamine* or *Smithsonite.* It may be prepared in the laboratory by reacting a solution of sodium bicarbonate with a solution of a zinc salt :

$$ZnSO_4 + 2NaHCO_3 = ZnCO_3 + CO_2 + H_2O + Na_2SO_4.$$

If a solution of sodium carbonate is used instead of sodium bicarbonate, the basic zinc carbonate, $2ZnCO_3.3Zn(OH)_2$ is precipitated. This happens because $Na_2CO_3$ hydrolyses in water and generates appreciable amounts of hydroxyl ions in solution, and these $OH^-$ ions produce $Zn(OH)_2$.

Zinc carbonate is a water-insoluble white powder. It decomposes on heating to ZnO and $CO_2$ : $ZnCO_3 = ZnO + CO_2$. It dissolves in acids, forming the zinc salts and liberating $CO_2$ :

$$ZnCO_3 + 2HCl = ZnCl_2 + CO_2 + H_2O.$$

**Complex Compounds of Zinc** : Zinc forms a large variety of complexes. In all the complexes, it exhibits bivalency and the common complexes are either 4-co-ordinated with $sp^3$-hybridisation (tetrahedral geometry), or 6-co-ordinated with $sp^3d^2$-hybridisation (octahedral geometry). The important complexes are the halo-complexes, $[ZnX_3]^-$, and $[ZnX_4]^{2-}$, where X=Cl, Br, or I. The ammine complexes include $[Zn(NH_3)_4]^{+2}$ and $[Zn(en)_2]^{+2}$ (where *en*=ethylenediamine). The acetylacetonate and dioxalate complexes of zinc are also well-characterised. The dialkyl sulphide addition-products of zinc halides, $(R_2S)_2\ ZnX_2$, and the thiourea complex, Zn (thiourea)$_2$Br$_2$, have also been isolated. The cyano-complexes, $[Zn(CN)_3]^-$ and $[Zn(CN)_4]^{2-}$ are well-known.

**Tests** : (i) All zinc salts, mixed with anhydrous $Na_2CO_3$ and heated on a charcoal-block in the reducing flame using a blow pipe, leave a residue which is yellow when hot, but white when cooled. The residue, on treatment with a drop of cobalt nitrate solution and then heating in the oxidising flame, changes into a green mass (Rinmann's green). (ii) Addition of a caustic soda solution to a zinc salt solution yields a white precipitate of $Zn(OH)_2$ which is soluble in excess of the alkali. (iii) When $H_2S$ is passed into ammoniacal solution of a zinc salt, a white precipitate of zinc sulphide is obtained. The precipitate is insoluble in ammonia or alkalis, but soluble in dilute mineral acids.

Zinc is estimated gravimetrically by precipitating it as zinc ammonium phosphate with a solution of disodium hydrogen phosphate in presence of $NH_4OH$ and $NH_4Cl$ ($pH = 6.6$). The precipitate is ignited (900°C) to zinc pyrophosphate and weighed as such. Volumetrically, zinc may be estimated by titration with a solution of potassium ferrocyanide potentiometrically or by using a standard E.D.T.A. solution using eriochrome black T as indicator.

## CADMIUM

*Symbol* : Cd ; *Atomic No.*=48 ; *Atomic wt.*=112·41

*Electronic configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2$.

**Occurrence** : Cadmium is generally found to accompany zinc in its ores, especially in *Calamine* and *Zinc blende*, to the extent of 0.2-0.5%, and the metal is invariably obtained from these sources. True cadmium ores are rare. The sulphide ore, **Greenockite** (CdS) and the oxide, CdO, are available very rarely. A basic carbonate ore (*Otavite*) has been reported from South West Africa.

**Extraction** : Cadmium is always extracted from the ores of zinc. Cadmium and its oxide (CdO) are more volatile than zinc (and ZnO), and are, therefore, considerably enriched (as CdO) in the zinc dust collected in the *receivers* during the distillation process of the extraction of zinc. Such zinc dust is mixed with powdered coke (to effect the reduction of CdO) and fractionally distilled several times at 800°-900°C. Enrichment of cadmium progressively takes place in the different fractions, and ultimately about 99.5% pure cadmium is obtained. [ZnO is not reduced or volatilised under these conditions.]

The above distillation process is often attended with considerable loss of Cd, as its vapours cannot be condensed easily. Such losses are avoided by the *wet extraction process*, in which the zinc dust, containing Cd, is dissolved in dil. HCl or $H_2SO_4$, and cadmium is deposited from the solution by adding metallic zinc : $Cd^{++} + Zn = Cd\downarrow + Zn^{++}$. The precipitated Cd is washed, dried and distilled at 800°-900°C to obtain very pure cadmium. Cadmium can also be extracted **electrolytically**, by a process essentially similar to the electrolytic extraction of zinc, described earlier. The zinc dust obtained in the receivers of the zinc distillation process is dissolved in dil. HCl or $H_2SO_4$, and the solution is electrolysed with platinum or cadmium cathode. Since the deposition potential of cadmium is much lower in magnitude than that of Zn (+0.4V for Cd and +0.76V for Zn), cadmium is selectively deposited at the cathode. A little gelatine or glue is added to the electrolytic bath to avoid the spongy deposits of cadmium.

Extremely pure cadmium (for use in standard cells) is prepared by repeated electrolytic refining and subsequent sublimation of the metal in hydrogen or in vacuum.

**Properties :** Cadmium is a soft, white, lustrous metal. It is malleable and very ductile. It readily tarnishes in air due to the formation of superficial film of the oxide. It melts at 321°C and boils at 767°C, and has a density of 8.64. It volatilizes above 800°C. Cadmium burns with a red flame when strongly heated in air, forming brown smokes of CdO. It also readily combines with sulphur and halogens when heated. Cadmium dissolves in dil. HCl and $H_2SO_4$ with the evolution of hydrogen, and in $HNO_3$ with the evolution of the oxides of nitrogen. It is unattacked by alkali solutions.

Uses : Cadmium is chiefly used for metallic coating as protection against corrosion. Its amalgam is used in Standard Weston Cell. The metal is also an ingredient of many useful alloys such as Wood's metal (Cd : Sn : Pb : Bi = 1 : 1 : 2 :4; melting at 71°C), rapid solder (50% Sn, 25% Pb, 25% Cd) melting at 149°C, amalgams for dental fillings *etc.*

## COMPOUNDS OF CADMIUM.

Cadmium compounds are similar to zinc compounds in all respects, and the metal invariably exhibits bivalency. The compounds of cadmium (except CdO and CdS, which are brown and yellow respectively) are colourless, unless the anions attached therein are coloured. [CdS is insoluble in dil. mineral acids in which ZnS is soluble.] All cadmium compounds have repulsive taste and are poisonous.

**Cadmium Hydride, $CdH_2$,** is obtained as a colourless solid on mixing at 70°C, an ethereal solution of $LiAlH_4$ to a solution of dimethyl cadmium in ether. The compound is not very stable.

**Cadmium Oxide and Hydroxide, CdO and $Cd(OH)_2$.**—The oxide is formed as an amorphous brown powder on burning the metal in air, or by the pyrolysis of its carbonate, nitrate or the hydroxide. It volatilises as a brown smoke at 700°C. It is a basic oxide, and is sparingly soluble in water and in alkalis, but dissolves in acids to form the corresponding salts. It is also soluble in ammonia solution, forming complex salts : $CdO + 4NH_4OH = [Cd(NH_3)_4](OH)_2 + 3H_2O$. The oxide is readily reduced by hydrogen at about 300°C and by carbon and carbon monoxide at higher temperatures.

The hydroxide is obtained as a white gelatinous precipitate by the addition of alkali solutions to those of cadmium salts. It is insoluble in water and alkalis, but is soluble in acids and ammonia solutions like the oxide. It is a rather strong base and absorbs $CO_2$ from air to form the carbonate.

[Cadmous oxide ($Cd_2O$), a yellow powder, may be prepared by melting a mixture of powdered cadmium metal and cadmium chloride ($CdCl_2$), and extracting the cooled melt with water, when cadmous hydroxide (CdOH) is precipitated. The washed and dried precipitate produces cadmous oxide.

$Cd+CdCl_2=2CdCl$ ;
$CdCl+H_2O=Cd(OH)\downarrow+HCl$
$2CdOH=Cd_2O+H_2O$.]

**Halides of Cadmium.**

**Cadmium Fluoride, $CdF_2$,** is formed as a colourless salt, on adding ammonium fluoride solution to a solution of cadmium chloride. It melts at 1110°C and has a density of 6.6. It is sparingly soluble in water and, unlike other cadmium halides, is not volatile.

**Cadmium Chloride, $CdCl_2$,** is obtained as the hydrated crystals of $2CdCl_2.5H_2O$, by dissolving the metal or its oxide, hydroxide or carbonate in HCl and concentrating the resultant solution. The anhydrous salt may be obtained by dehydrating (120°C) the hydrated salt, or by heating the metal or its oxide in chlorine. It is colourless (density=4.05, m.p. 565°C, b.p. 964°C of the anhydrous salt) and is very soluble in water. It is a weak electrolyte and this behaviour is ascribed to the formation of auto-complex in aqueous solution. $2CdCl_2 \rightleftharpoons Cd[CdCl_4]$.

**Cadmium Bromide, $CdBr_2$,** is similar to $CdCl_2$ in every respect and is similarly prepared. The anhydrous salt (density=5.2) melts at about 570°C and boils at 863°C.

**Cadmium Iodide, $CdI_2$,** is only known in the anhydrous state. It may be obtained as colourless, shining crystals, by the action of iodine on cadmium in the presence of water, or by dissolving the oxide or the carbonate of the metal in hydroiodic acid. It has a density of 5.7, melts at about 385°C and boils at 708-719°C. It is soluble in water and also in organic solvents like alcohol and acetone. It has been definitely known from measurements of conductivity, osmotic pressure, electrode potentials, transport numbers, boiling point and freezing point that, $CdI_2$ exists in aqueous solutions largely in the form of **auto-complexes**, such as $Cd[CdI_3]_2$, $Cd[CdI_4]$ *etc.*

$3CdI_2 \rightleftharpoons Cd[CdI_3]_2 \rightleftharpoons Cd^{++}+2[CdI_3]^-$ ;
$2CdI_2 \rightleftharpoons Cd[CdI_4] \rightleftharpoons Cd^{++}+[CdI_4]^{2-}$.

Cadmium iodide also forms crystals of double or complex iodides such as $K[CdI_3]$, $K_2[CdI_4]$, $K_4[CdI_6]$ *etc.*

**Cadmium Carbonate, $CdCO_3$,** is thrown down as a white precipitate, on adding solutions of alkali carbonates to cadmium salt solutions. It is commonly admixed with some $Cd(OH)_2$. Pure cadmium carbonate is prepared by adding a solution of ammonium carbonate to a solution of $CdCl_2$. The precipitate formed (of impure cadmium carbonate) is dissolved in requisite amount of $NH_4OH$ solution. The resultant solution, on concentration on water bath, produces small crystals of the pure carbonate. It is sparingly soluble in water and alkali solutions, but is decomposed by acids, with the evolution of $CO_2$. It also decomposes to CdO and $CO_2$ on heating above 350°C.

**Cadmium Cyanide,** $Cd(CN)_2$, is formed as a white precipitate on adding a solution of alkali cyanide to cadmium salt solutions. It is decomposed and dissolved by strong mineral acids. It also dissolves in excess of alkali cyanide solutions to form complex ion, $[Cd(CN)_4]^{2-}$, whose crystalline alkali salts have been isolated. A solution of alkali cadmicyanide like $K_2[Cd(CN)_4]$ is decomposed to precipitate yellow CdS on passing $H_2S$ gas. (This reaction is utilised to differentiate $Cu^{++}$ and $Cd^{++}$ in qualitative analysis.)

**Cadmium Sulphide, CdS,** occurs in nature as *Greenockite.* It is precipitated as a bright yellow solid when an acidified solution of a cadmium salt is saturated with $H_2S$. It is insoluble in water and dil. HCl, but is soluble in warm dil. $HNO_3$, boiling dil. $H_2SO_4$ (1 : 5) and in concentrated acids. It is insoluble in yellow ammonium sulphide as well. Cadmium sulphide is used as a valuable artists' pigment for its brilliancy and permanency.

**Cadmium Sulphate,** $CdSO_4$, is formed by dissolving the metal or its oxide or carbonate in dil. $H_2SO_4$. The solid salt is crystallised as $3CdSO_4.8H_2O$, by concentrating these solutions. It is a colourless compound, soluble in water, and is, therefore, used as the starting material for the preparation of other cadmium compounds. It begins to volatilise when heated above 700°C, with partial decomposition. Above 1000°C, it is decomposed completely to form CdO and $SO_3$. A solution of the compound in aqueous ammonia gives complex ammines on concentration. Cadmium sulphate forms double sulphates with the sulphates of alkali metals. It is used in Weston cell and also in medicine.

**Cadmium Nitrate,** $Cd(NO_3)_2$, is most readily obtained by dissolving CdO or $CdCO_3$ in dil. $HNO_3$. The solution, on crystallisation at ordinary temperatures, gives the crystals of the tetrahydrate, $Cd(NO_3)_2.4H_2O$, which dissolves in their own water of crystallisation at 59.3°C. It is deliquescent and highly soluble in water. It is decomposed on heating to give CdO.

Tests : (i) Cadmium is precipitated as yellow CdS from an acidic solution of its salts, on passing $H_2S$. The ppt. is insoluble in yellow ammonium sulphide or alkalis, but is soluble in warm, dil. $HNO_3$. Gravimetrically, it is estimated by deposition from cyanide solutions of its salts and weighed as such.

## MERCURY

*Symbol* : Hg ; *Atomic No.*=80 ; *Atomic weight*=200.61.

*Electronic configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2$.

**OCCURRENCE** : The principal ore of mercury is *cinnabar* (mercuric sulphide, HgS, red or black), occuring mainly in Spain, and also in smaller quantities in Italy, Yugoslavia, U.S.A., U.S.S.R., Mexico and Canada. The mercury-content of the ore varies from 1—6%. Mercury also occurs native (as small droplets), although such occurrence is rare. Other minor deposits of the metal as selenide (*Tiemannite*, HgSe), telluride (*Coloradoite*, HgTe) or oxide (HgO) are available, but they have no commercial importance.

**EXTRACTION** : In the older Spanish Process (which is still used at some places), the ore (cinnabar) is first crushed and concentrated. The concentrated ore is then roasted in a current of air at 600—700°C, when $SO_2$ and vapours of the metal are formed. The vapours of the metal are condensed to get the liquid metal :

$$HgS+O_2=Hg+SO_2.$$

Alternatively, the concentrated ore may be roasted with iron scraps or lime (CaO), when the non-volatile products are retained in the furnace and the vapours of mercury that issue out are condensed in a series of *aludels* (small clay receptacles) : $HgS+Fe=Hg\uparrow+FeS$ ; $4HgS+4CaO=4Hg\uparrow+3CaS+CaSO_4$. In the modern process, the metal is extracted by heating a mixture of powdered cinnabar and coke in a long shaft furnace. The charge is fed at the top of the furnace through a *cup-and-cone* arrangement and hot air is blown from near the bottom. The hot air-blast causes coke to burn ; the resultant heat decomposes cinnabar to mercuric oxide and ultimately to metallic

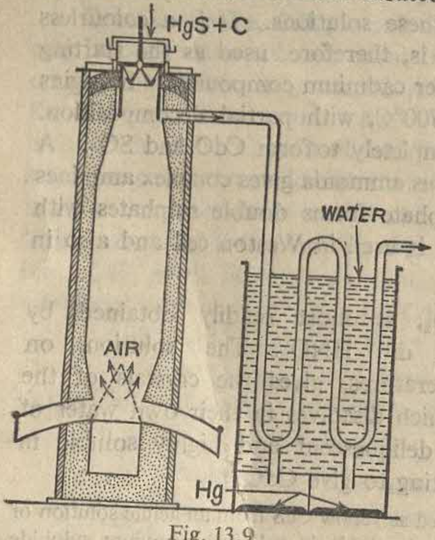


Fig. 13.9

mercury. A portion of the mercuric oxide formed is also reduced by the glowing carbon particles to the metallic state, producing carbon monoxide : $2HgS+3O_2=2HgO+2SO_2$ ; $2HgO=2Hg+O_2$ ; $HgO+C=Hg+CO$. The vapours of mercury, along with $SO_2$, CO and excess of air, escape through an exit pipe near the top of the furnace, and the gaseous mixture is then passed through a number of iron pipe condensers cooled in a water-tank, as shown in Fig. 13.9. Mercury condenses and collects at the bottom of the tank, while the gases escape outside.

**Purification of mercury** : The crude metal obtained above (or the metal available commercially) is filtered by pressing through chamois leather or fine canvas to remove suspended impurities. The dissolved impurities (such as the less noble metals like Mg, Al, Cr, Mn, Cd, Sn, Pb, Ni, Cu *etc.*) are then removed by running the metal in a thin stream through a long tube (Fig. 13.10), containing dil. $HNO_3$ and a little mercurous nitrate. The impurities are either dissolved or oxidised by this process. Mercury is then filtered again, dried and distilled under reduced pressure, when more than 99.9% pure metal is obtained.

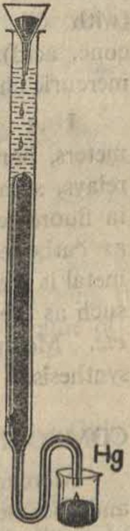


Fig. 13.10

**Properties** : Mercury is a heavy (density=13.5), glistening silvery liquid which boils at 357°C and can be frozen to a solid at—39°C. Solid mercury is soft and ductile. It is the only metal which is liquid at ordinary temperatures. It is perceptibly volatile at ordinary temperatures, and its vapours are monatomic and highly poisonous. It is not a very good conductor of heat and electricity. It can be readily emulsified by rubbing with fat, and can be dispersed to a black powder (*deadening of mercury*) by shaking vigorously (either alone or in presence of sugar). Mercury forms alloys (*amalgams*) with many metals (exceptions are Pt, Fe, Co, Ni, Mn).

Mercury does not react appreciably with air or oxygen at room temperature ; but, on heating to about 350°C, mercuric oxide (HgO) is formed, which decomposes into the constituent elements on stronger heating (about 500°C or above). All the halogens react directly with the metal at ordinary temperatures ; mercurous halides seem to be first formed, followed by the formation of mercuric halides, if halogen is in excess : $2Hg+X_2=Hg_2X_2$ ; $Hg_2X_2+X_2=2HgX_2$ (X=halogen). [Sometimes, the reaction is slowed down by the formation of a protective coating of insoluble salts.] Sulphur reacts with mercury, on rubbing or heating them together, to give black mercuric sulphide (HgS). Ozone readily reacts with the metal at room temperature, whereby the mobility of mercury is lost (probably due to the formation of oxide). Nitrogen dioxide very rapidly reacts with the metal to give a mixture of mercuric nitrate and mercurous nitrate. Dil. HCl or $H_2SO_4$ do not react with mercury ; moderately concentrated acids ($>$6N) attack the metal superficially to give a little amount of mercurous salts. Hot conc. $H_2SO_4$ dissolves mercury to give mercuric sulphate and $SO_2$ : $Hg+2H_2SO_4=HgSO_4+SO_2+2H_2O$. Nitric acid reacts with the metal to give products which depend upon the concentration of the acid : $6Hg+8HNO_3=3Hg_2(NO_3)_2+2NO+4H_2O$ (with dil. acid) ; $3Hg+8HNO_3=3Hg(NO_3)_2+2NO+4H_2O$ (with conc. acid). Mercury dissolves very readily in aqua regia, forming mercuric chloride.

**Uses :** Mercury is used in many scientific apparatus like thermometers, barometers, diffusion pumps, gas-pressure regulators, electric relays, standard cells, temperature-compensating pendulums *etc.* and in fluorescent lights, street-lights, A.C. rectifiers *etc.* It is also used as cathode in the electrolytic manufacture of caustic soda. The metal is used for the preparation of many of its important compounds such as the red sulphide (*vermillion*), mercury fulminate (an *explosive*) *etc.* Mercury and its salts are sometimes used as catalysts in organic synthesis.

## COMPOUNDS OF MERCURY.

Mercury forms two distinct series of simple salts, *viz.* the **mercurous** and the **mercuric** salts. The metal appears to exhibit monovalency in the mercurous salts. But, it has been shown that the constitution of a mercurous salt should be represented by two atoms of the metal, linked together in a molecule, as X-Hg-Hg-X (X=a monovalent anion). The molecular formula of such a compound should, therefore, be double its empirical formula, HgX. Mercury is thus formally **bivalent**, although electrochemically **unipositive** in the mercurous salts. Many evidences have been put forward to point to the binuclear nature of $Hg_2^{++}$ ion. Of these, only some important ones are mentioned below :

(i) The X-ray structures of many mercurous salts have shown that mercury atoms in their crystals are always associated in pairs with almost constant Hg—Hg bond distance (2.5—2.6Å).

(ii) Mercurous compounds are diamagnetic both in the solid state and in solution. Had these compounds contained $Hg^+$ ions, they would have been paramagnetic.

(iii) The Raman spectrum of aqueous solution of mercurous nitrate indicates the existence of Hg—Hg bond.

(iv) The vapour density of pure and dry mercurous chloride (236) gives its molecular weight as 472, which is in accord with the formula $Hg_2Cl_2$. The lowering of the freezing point of a dilute solution of mercurous nitrate also indicates its formula as $Hg_2(NO_3)_2$.

(v) The measurement of the e.m.f. of a **concentration cell,** containing mercurous nitrate of two different concentrations (in $\frac{N}{10}$ $HNO_3$) with mercury electrodes was carried out to find out the valency of Hg in the salt, by applying the equation, $E = \frac{2.303RT}{nF} \log \frac{C_1}{C_2}$ (where E is the measured e.m.f., $n$ is the valency of Hg, $C_1$ and $C_2$ and the two concentrations of mercurous nitrate and R, T and F have usual significance). The value of $n$ was calculated to be 2, which confirmed the existence of $Hg_2^{++}$ ions.

(vi) Various equilibria, as shown below, were studied and the equilibrium constant (K) was evaluated in each case, supposing the formation of either $Hg^+$ or $Hg_2^{++}$ ; it was found that the value of K was constant only if the formation of $Hg_2^{++}$ was considered :

(a) $Hg^\circ + Hg^{++} \rightleftharpoons Hg_2^{++}$, or $Hg^\circ + Hg^{++} \rightleftharpoons 2Hg^+$ ;
(b) $2Hg^\circ + 2Ag^+ \rightleftharpoons 2Ag^\circ + Hg_2^{++}$, or $Hg^\circ + Ag^+ \rightleftharpoons Ag^\circ + Hg^+$.

(vii) It was observed that, if the influence of hydrolysis is eliminated, the electrical conductivity of soluble mercurous salts corresponds to that of typical bi-univalent electrolytes [like $Ba(NO_3)_2$], and not to uni-univalent salts (like $KNO_3$).

### Mercury (I) Compounds.

**Mercurous Oxide** ($Hg_2O$).—The existence of this oxide has not been definitely proved. The earlier report on the isolation of $Hg_2O$ by the action of alkali solutions on solutions of mercurous salts has been found to be incorrect, as the product proved to be a mixture of Hg and HgO.

**Mercurous Chloride,** (**Calomel,** $Hg_2Cl_2$), is obtained by heating an intimate mixture of mercuric chloride (*corrosive sublimate*, $HgCl_2$) and metallic mercury, or a mixture of mercuric sulphate, mercury and common salt (NaCl). The product sublimes off, and is collected by cooling as white glistening crystals : $HgCl_2+Hg=Hg_2Cl_2$ ; $HgSO_4+Hg+2NaCl=Hg_2Cl_2+Na_2SO_4$.

Mercurous chloride is also formed as a white precipitate when mercuric chloride is reduced by $SO_2$, or dil. HCl is added to a solution of mercurous nitrate : $2HgCl_2+SO_2+2H_2O=Hg_2Cl_2+H_2SO_4+2HCl$ ; $Hg_2(NO_3)_2+2HCl=Hg_2Cl_2+2HNO_3$.

Mercurous chloride sublimes at 383°C without melting. It is sparingly soluble in water and organic solvents, but is appreciably soluble in a solution of a chloride. It turns yellow on heating and darkens on exposure to light,—probably due to partial decomposition into mercuric chloride and metallic mercury. It turns black when treated with ammonia. The black colour is assumed to be due to the formation of a mixture of amido-mercuric chloride ($NH_2HgCl$) and finely divided mercury :

$$Hg_2Cl_2+2NH_4OH=NH_2HgCl+Hg+NH_4Cl+2H_2O.$$

Mercurous chloride is insoluble in dil. HCl or $HNO_3$. But, in concentrated acids and in aqua regia, it gives the following reactions :

$$Hg_2Cl_2+2HCl=Hg\downarrow+H_2[HgCl_4]\ ;$$

$$3Hg_2Cl_2+8HNO_3=3HgCl_2+3Hg(NO_3)_2+2NO+4H_2O\ ;$$

$$Hg_2Cl_2+2[Cl]\ (\text{aqua regia})=2HgCl_2\ :$$

It is reduced to the metal (often formed as a grey mirror), when heated with anhydrous $Na_2CO_3$ ;

$$2Hg_2Cl_2+2Na_2CO_3=4Hg+4NaCl+2CO_2+O_2.$$

It is used in medicine as purgative. Calomel electrodes are also prepared from this compound.

**Mercurous Fluoride, $Hg_2F_2$,** is obtained by dissolving freshly prepared mercurous carbonate in hydrofluoric acid. It is a light yellow powder which is more soluble in water than the chloride, and suffers hydrolysis in aqueous solution. It turns black on exposure to light, due to decomposition.

**Mercurous Bromide, $Hg_2Br_2$,** is formed as a white solid on adding potassium bromide solution to a solution of mercurous nitrate. It resembles the chloride in properties.

**Mercurous Iodide, $Hg_2I_2$,** is formed as a green precipitate on adding a little alkali iodide to mercurous nitrate solution, or as a greenish yellow powder by rubbing mercury with iodine in presence of a little alcohol. It is practically insoluble in water and readily decomposes into mercury and mercuric iodide. When it is treated with alkali iodide solution, half of the mercury goes into solution as a complex of bivalent mercury and the other half is reduced to metallic mercury : $Hg_2I_2+2KI=K_2[HgI_4]+Hg$.

**Mercurous Carbonate, $Hg_2CO_3$,** is precipitated as a yellow compound on adding alkali carbonate solution to a solution of mercurous salt. It is sparingly soluble in water and readily decomposes into Hg, HgO and $CO_2$.

**Mercurous Nitrate, [$Hg_2(NO_3)_2$]**, is prepared by the action of dilute $HNO_3$ on excess of mercury. It is also obtained by the action of metallic mercury on mercuric nitrate solution : $6Hg+8HNO_3=3Hg_2(NO_3)_2+4H_2O+2NO$ ; $Hg(NO_3)_2+Hg=Hg_2(NO_3)_2$.

Mercurous nitrate is obtained as efflorescent, colourless crystals, having the composition, $Hg_2(NO_3)_2.2H_2O$. It slightly decomposes when melted (m.p. 70°C). The salt is soluble in water, the aqueous solution being acidic due to hydrolysis. Heating of the dilute solutions precipitates the lemon-yellow basic salt, $Hg_2(NO_3)(OH)$ : $Hg_2(NO_3)_2+H_2O \rightleftharpoons Hg_2(NO_3)(OH)+HNO_3$. On strongly heating, the solid salt decomposes into mercuric oxide and nitrogen dioxide : $Hg_2(NO_3)_2=2HgO+2NO_2$. It is readily oxidised when exposed to air and is, therefore, stored over metallic mercury to prevent aerial oxidation.

**Mercurous Sulphate, $Hg_2SO_4$**, is obtained by adding dil. $H_2SO_4$ to a solution of mercurous nitrate, or by heating an excess of mercury with conc. $H_2SO_4$. It forms colourless crystals, sparingly soluble in water and dil. $H_2SO_4$. It is gradually decomposed by water to give the greenish yellow, insoluble basic salt. It darkens on exposure to light. Mercurous sulphate is used as a catalyst for the oxidation of many organic substances and also in the Kjeldahl's method of estimation of nitrogen and in Weston cell.

### Mercury (II) Compounds.

**Mercuric Oxide, (HgO)**, is precipitated as a yellow substance on adding excess of an alkali solution to a solution of mercuric chloride or nitrate. A red crystalline variety of the compound is prepared by gently heating solid mercuric or mercurous nitrate : $HgCl_2+2NaOH=HgO+2NaCl+H_2O$ ; $2Hg(NO_3)_2=2HgO+4NO_2+O_2$ ; $Hg_2(NO_3)_2=2HgO+2NO_2$. Heating the metal in oxygen at about 300°C also produces the red mercuric oxide. [The red and the yellow forms of HgO differ only in the size of the particles of the solid material. The yellow variety is the more finely divided form of the red variety.]

Mercuric oxide decomposes into mercury and oxygen before melting. It is a weak base and an oxidising agent. Stronger acids dissolve the oxide to form the mercuric salts : $HgO+2HNO_3=Hg(NO_3)_2+H_2O$. It also reacts with halogens to form halides and halates (oxygen is also formed in some cases). When dry $Cl_2$ is passed over cooled precipitated HgO, chlorine monoxide is formed : $2Cl_2+2HgO=HgO.HgCl_2+Cl_2O$. [Chlorine monoxide dissolves in water to give hypochlorous acid : $Cl_2O+H_2O=2HOCl$.] A suspension of mercuric oxide in water dissolves on adding KI solution to form the soluble complex potassium mercuri-iodide, $K_2[HgI_4]$, and liberating free alkali : $HgO + 4KI + H_2O = K_2[HgI_4] + 2KOH$. The oxide may, therefore, be used as a primary standard in acidimetric titrations.

Mercuric oxide is used to prepare mercuric salts and hypochlorous acid. It also finds some application in medicine.

**Mercuric Chloride** (*Corrosive sublimate*, $HgCl_2$) is prepared by heating an intimate mixture of mercuric sulphate and common salt (NaCl). The sublimed product is collected, on cooling, as white transparent crystals. It is also obtained by dissolving HgO in HCl, and evaporating the solution to crystallisation : $HgSO_4+2NaCl=Na_2SO_4+HgCl_2$ ; $HgO+2HCl=HgCl_2+H_2O$.

A white, crystalline substance of density 5.44, mercuric chloride melts at 280°C and boils at 302°C. It is sublimable, and is not affected by light. The compound is fairly soluble in water and alcohol, and is highly poisonous. The covalent nature of mercuric chloride is manifested in its lower boiling point, greater solubilities in alcohol and ether than in water. It reacts with boiling ammonia solution to give amido-mercuric chloride, $(NH_2.HgCl)$, commonly known as the *infusible white precipitate* : $HgCl_2+2NH_3=NH_4Cl+NH_2.HgCl$. It is reduced by stannous chloride to grey metallic mercury, through the intermediate formation of mercurous chloride : $2HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4$ ; $Hg_2Cl_2+SnCl_2=2Hg+SnCl_4$. When a solution of KI is added to a solution of mercuric chloride, a red precipitate of mercuric iodide ($HgI_2$) is first formed ; this dissolves on adding excess of KI solution to form a colourless solution, containing the complex salt, potassium mercuri-iodide : $HgCl_2+2KI=2KCl+HgI_2\downarrow$ ; $HgI_2+2KI=K_2[HgI_4]$. If a clean copper wire or strip is dipped into a solution of mercuric chloride, metallic mercury is deposited as a grey substance on the copper wire or strip : $HgCl_2+Cu=CuCl_2+Hg$. When dry mercuric chloride is heated with excess of anhydrous $Na_2CO_3$, it is reduced to the metal, forming a grey mirror on the inner wall of the test tube in which the heating is performed : $2HgCl_2+2Na_2CO_3=2Hg+4NaCl+2CO_2+O_2$.

Mercuric chloride is used in medicine and as an antiseptic and disinfectant. It is also used in protecting wood, and in photography.

**Mercuric fluoride, $HgF_2$,** is essentially ionic compound. The yellow hydrated salt, $HgF_2.2H_2O$, is obtained by dissolving HgO in hydrofluoric acid and concentrating the resultant solution. The white anhydrous salt may be obtained by dehydrating the hydrated salt, or by heating mercurous fluoride in chlorine at 275°C (or alone in vacuum at 450°C) : $HgO+2HF=HgF_2+H_2O$ ; $Hg_2F_2+Cl_2=HgF_2+$

$HgCl_2$; $Hg_2F_2 = HgF_2 + Hg$. It is soluble in water, but is extensively hydrolysed in aqueous solution to give basic fluoride, Hg(OH)F first and ultimately HgO. It does not give any fluoro-complex with HF or akali fluoride solutions.

**Mercuric Bromide, $HgBr_2$,** resembles mercuric chloride in properties and is similarly prepared. It is rather less soluble in water than the chloride and is even more weakly dissociated in solution. It dissolves in alkali chloride and bromide solutions to give complex salts.

**Mercuric Iodide, $HgI_2$,** is obtained as a red powder by precipitation from a solution of mercuric nitrate with a small amount of KI solution, or by rubbing requisite amounts of mercury and iodine with a little alcohol. It is sparingly soluble in water, but is more soluble in alcohol and some other organic solvents. The compound is dimorphous, changing to the yellow form above 126°C ; the change being reversible. It dissociates to a still smaller extent than the other mercuric halides and, in fact, its solution gives no precipitate of AgI when treated with $AgNO_3$ solution. It does not also form oxide or basic salts on addition of alkalis in the cold. Mercuric iodide dissolves in excess of KI solution to give an almost colourless solution of the iodo-complex $K_2[HgI_4]$, potassium tetraiodo-mercurate. An alkaline (NaOH or KOH) solution of this complex is used to detect ammonia or ammonium salts under the name **Nessler's Reagent.** The reagent gives brown colour or precipitate ($NH_2Hg_2I_3$) with ammonia or ammonium salts. Mercuric iodide also dissolves in mercuric chloride solution to give mercuric chloroiodide, $Hg_2I_2Cl_2$.

**Mercuric Carbonate :** Neutral mercuric carbonate cannot be prepared. Basic carbonates of variable compositions are formed when mercuric nitrate solution is treated with alkali carbonates or bicarbonates.

**Mercuric Cyanide, $Hg(CN)_2$,** is obtained by the action of aqueous HCN on HgO, or by adding alkali cyanide solution to a solution of mercuric nitrate. [The reaction between alkali cyanide and mercurous nitrate solutions gives mercuric cyanide together with metallic Hg.]

Mercuric cyanide is a colourless, odourless, crystalline compound, fairly soluble in water, but not in alcohol. Its aqueous solution does not give a precipitate of HgO when treated with alkali solutions, but $H_2S$ precipitates from it the black mercuric sulphide (HgS). When the dry salt is heated to 320°C, it decomposes to mercury and cyanogen gas. It forms many strong complexes with alkali metal cyanides.

Mercuric cyanide is highly poisonous. It has some therapeutic use and is also used as a disinfectant.

**Mercuric Cyanate, $Hg(ONC)_2$,** also known as **mercury fulminate,** is precipitated by adding a solution of potassium cyanate to a solution of mercuric nitrate. It is a white powder, insoluble in water. It is a very strong explosive and is used in detonators.

**Mercuric Thiocyanate, $Hg(SCN)_2$,** is obtained as a white precipitate on adding potassium thiocyanate solution to a solution of mercuric nitrate. It is sparingly soluble in cold water, but is more soluble in hot water and alcohol. The dry salt swells up to large bulk when ignited, and the small pellets of it are commonly sold under the name *Pharaoh's serpent* as fireworks. It dissolves in excess of potassium thiocyanate solution to form complex thiocyanates of the type $K_2[Hg(SCN)_4]$. The $Zn^{++}$, $Ni^{++}$, $Co^{++}$, $Fe^{++}$ salts of the complex thiocyanate have also been isolated.

**Mercuric Nitrate, $Hg(NO_3)_2$,** is easily prepared as colourless, deliquescent crystals of the monohydrate, $Hg(NO_3)_2.H_2O$, by dissolving metallic mercury (or HgO) in excess of $HNO_3$ and evaporating the resultant solution to crystallisation. The monohydrate forms the basic salt on heating. The anhydrous salt is, therefore, prepared by the action of $N_2O_4$ on HgO.

Mercuric nitrate is hydrolysed by water even at 25°C, to form an insoluble, white precipitate of the basic nitrate, which on further heating with water, gives HgO :

$$Hg(NO_3)_2+H_2O=Hg(OH)(NO_3)+HNO_3\ ;$$
$$Hg(OH)(NO_3)=HgO+HNO_3.$$

Mercuric nitrate is the starting material for the preparation of many mercuric compounds.

**Mercuric sulphide (HgS)** occurs in two varieties—red and black. The red sulphide occurs naturally as the ore *cinnabar* ; the black variety also accompanies *cinnabar* as *meta-cinnabarite* in small amounts. The red variety is formed on passing $H_2S$ through a solution of mercuric acetate in glacial acetic acid (containing some ammonium thiocyanate). It is also obtained by the direct union of mercury and sulphur on heating, or by heating a mixture of mercury and potassium pentasulphide. The black variety is formed on passing $H_2S$ into a solution of $HgCl_2$ in dil. HCl, or by rubbing mercury and powdered sulphur together in a mortar. The black variety changes to the red one on sublimation.

Mercuric sulphide is practically insoluble in water and is not acted upon by most of the acids (except HBr, HI and *aqua regia*). It is soluble in a solution of alkali metal sulphides to form thio-salts : $HgS+K_2S=K_2[HgS_2]$. Halogens react with mercuric sulphide slowly, forming mercuric halides and liberating sulphur. On heating in oxygen or air, mercuric sulphide is oxidised to give a mixture of Hg, $Hg_2SO_4$, $HgSO_4$ and $SO_2$. It can be reduced to the metallic state by heating in a current of hydrogen at 400°C : $HgS+H_2=Hg+H_2S$. Mercury is set free when mercuric sulphide is strongly heated with iron powder : $HgS+Fe=FeS+Hg$.

Red mercuric sulphide is used as *vermillion.* In the black form or the red form, it is widely used in Ayurvedic medicine as *Kajjali* and *Makaradhwaja* respectively.

**Mercuric sulphate, ($HgSO_4$),** is obtained by dissolving HgO in $H_2SO_4$, or by the repeated evaporation of mercury with an excess of conc. $H_2SO_4$. The anhydrous salt is a colourless, crystalline solid which forms crystals of the monohydrate, $HgSO_4.H_2O$, on addition of a small amount of water. It is hydrolysed by a large volume of water to the yellow basic sulphate. The salt is decomposed into Hg, $SO_2$ and $O_2$, when heated strongly.

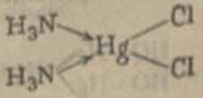
Mercuric sulphate is industrially used as a catalyst for preparing acetaldehyde from acetylene.

**Ammonia-Mercury Compounds.**

It has already been stated that mercurous chloride turns black when treated with aqueous ammonia, due to the formation of amidomercuric chloride (mercurous salt is oxidised to mercuric salt) and metallic mercury. The reaction is often used to identify $Hg_2Cl_2$. The reactions of ammonia with mercuric chloride are, however, interesting and important. These reactions distinguish mercury from its congeners, *viz.* zinc and cadmium which do not give these reactions.

There are three different known products of the reaction of $HgCl_2$ with ammonia, and their formation and proportions depend on the conditions of the reactions. It appears from the products of these reactions that mercury can not only add ammonia to some of its compounds, but is also able to replace the hydrogen of ammonia.

(*i*) The most important of the ammonia addition-compounds is the **fusible white precipitate.** When ammonia gas is passed over $HgCl_2$, or if a boiling solution of mercuric chloride, containing much $NH_4Cl$, is treated with $NH_4OH$, a white crystalline precipitate of composition $HgCl_2.2NH_3$, is obtained. This is called *fusible white precipitate*, as it can be **melted** (with decomposition) when heated. The compound readily dissolves in $HNO_3$ and $H_2SO_4$ to form a mixture of mercuric chloride and the ammonium salt of the acid concerned. It is regarded as a coordination compound, *viz. diamminemercuric chloride* and is represented as in the margin.



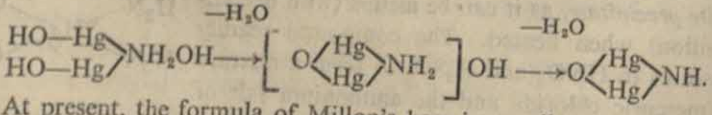
The tetrammine salt, $[Hg(NH_3)_4]Cl_2$ has also been prepared by the action of ammonia on mercuric salts suspended in saturated $NH_4Cl$ solution.

(*ii*) When ammonium hydroxide is added to a dilute solution of mercuric chloride which contains little or no $NH_4Cl$, a white precipitate, called **infusible white precipitate**, is formed. Its formula is given by $NH_2.HgCl$ (amido-mercuric chloride) : $HgCl_2+2NH_3=NH_2.HgCl+NH_4Cl$.

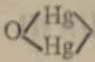
This compound decomposes, when heated, **without melting** into $Hg_2Cl_2$, $NH_3$ and $N_2$. It is, therefore, so named. It is insoluble in water, but soluble in dil. mineral acids in presence of a little NaCl. When boiled with KOH solution, all the nitrogen contained in the compound is liberated as $NH_3$. All the chlorine in the compound can be precipitated as AgCl. The corresponding bromine compound is also known.

(*iii*) When mercuric oxide is heated with ammonium hydroxide solution, a bright yellow, micro-crystalline powder, having the composition $Hg_2NH_5O_3$, is obtained. It is known as **Millon's base.** It is a well-defined compound and loses a molecule of water on dehydration over KOH in an atmosphere of ammonia to give a dark yellow powder of composition $Hg_2NH_3O_2$, which forms salts of composition $[Hg_2NH_2O]X$ (where X is a halogen or other monovalent anions). This was, therefore, respresented (Hofmann, 1899) as $\left[O\begin{matrix}\diagup Hg\diagdown\\ \diagdown Hg\diagup\end{matrix}NH_2\right]OH$, and the salts as $\left[O\begin{matrix}\diagup Hg\diagdown\\ \diagdown Hg\diagup\end{matrix}N\,H_2\right]X$. Millon's base was represented by Hofmann as *dihydroxy mercury* (II) *-ammonium hydroxide*, $\left[\begin{matrix}HO{-}Hg\diagdown\\ HO{-}Hg\diagup\end{matrix}NH_2\right]OH$.

$Hg_2NH_3O_2$ lost a further molecule of water, when heated to 125°C in a current of ammonia, to give a dark brown powder of composition $Hg_2NHO$. This was represented by Hofmann as $O\begin{matrix}\diagup Hg\diagdown\\ \diagdown Hg\diagup\end{matrix}NH$, and it no longer has the property of forming salts. The course of the dehydration is represented as :



$$\begin{matrix}HO{-}Hg\diagdown\\ HO{-}Hg\diagup\end{matrix}NH_2OH\xrightarrow{-H_2O}\left[O\begin{matrix}\diagup Hg\diagdown\\ \diagdown Hg\diagup\end{matrix}NH_2\right]OH\xrightarrow{-H_2O}O\begin{matrix}\diagup Hg\diagdown\\ \diagdown Hg\diagup\end{matrix}NH.$$

At present, the formula of Millon's base is usually accepted as a monohydrate, *viz.* $HO{-}Hg{-}O{-}Hg{-}NH_2.H_2O$, which on dehydration over KOH (in $NH_3$-atmosphere) forms HO—Hg—O—Hg—$NH_2$, and this, on further dehydration, gives $OHg_2NH$, which may have the cyclic structure  $O\langle{}^{Hg}_{Hg}\rangle NH$, or a structure of high molecular complexity. It has been shown that Millon's base has a structure of a three-dimensional framework of composition $Hg_2N$, with the $OH^-$ ions and $H_2O$ molecules occupying rather spacious cavities and channels.

The above three types of ammonia-mercury compounds are connected by the following reactions :

$$\underset{\text{Chloride of Millon's base}}{Cl{-}Hg{-}O{-}Hg{-}NH_2} + NH_4Cl \rightleftharpoons \underset{\text{Amido-mercuric chloride}}{2Cl{-}Hg{-}NH_2} + H_2O\ ;$$

$$Cl{-}Hg{-}NH_2 + NH_4Cl \rightleftharpoons \underset{\text{Diamminemercuric chloride}}{[Hg(NH_3)_2]Cl_2}$$

The brown compound that is formed by the interaction of ammonia (or ammonium salts) with the Nessler's reagent (alkaline solution of potassium mercuri-iodide) is the iodide of Millon's base :

$$2K_2[HgI_4] + NH_3 + 3KOH = [NH_2{-}Hg{-}O{-}Hg]I + 7KI + 2H_2O.$$

Tests : (i) Mercury compounds, when heated with anhydrous sodium carbonate, give grey sublimate (or mirror) of mercury. (ii) When a clean copper strip is dipped in a dilute solution of mercury salt, mercury is deposited on the copper strip. To distinguish mercuric and mercurous salts, the following tests are done in solution :

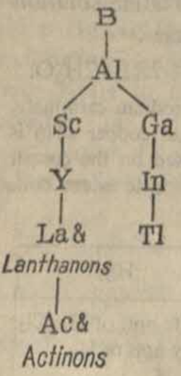
| Reagent | $Hg^{++}$ | $Hg_2^{++}$ |
|---|---|---|
| (i) Dil. HCl | No. ppt. | White ppt. of $Hg_2Cl_2$ |
| (ii) $H_2S$ gas passed | Black ppt. of HgS is ultimately formed. | Grey ppt. of Hg. |
| (iii) KI soln. | Red ppt. of $HgI_2$, soluble in exces of KI solution. | Green ppt. of $Hg_2I_2$. |
| (iv) NaOH soln. | Yellow ppt. of HgO. | Black ppt. |
| (v) $NH_4OH$ soln. | White ppt. | Black ppt. |

In gravimetric analysis, mercurous and mercuric salts are precipitated as $Hg_2Cl_2$ and HgS respectively and are weighed as such after proper washing and appropriate drying. It is also estimated by electrolytically depositing as the metal.

CHAPTER XIV

# ELEMENTS OF GROUP III

Group III is the largest of all the groups of the Periodic Table. In fact, this group contains 37 elements, and as is the case with other groups of the Table, it is sub-divided into sub-groups A and B. Boron and aluminium are the two typical elements of this group, occuring in the 1st and the 2nd short periods respectively of the Periodic Table. Along with its three congeners, *viz*. gallium, indium and thalium, they form the B sub-group of Group III, and is considered as the main sub-group of this group. The sub-group A of this group starts with scandium (Sc) and is followed by yttrium (Y) and lanthanum (La), together with 14 **lanthanide elements** or **lanthanons** (Ce to Lu), which are very similar to lanthanum and among themselves. These 14 elements (which are all transition metals) are popularly known as the **rare-earth elements.** The electronic configuration of the outermost shell of the rare-earth elements is the same, containing 3 electrons, and with the increase of atomic number, their inner 4*f* shell is gradually filled up by electrons. They generally exhibit tervalency (hence placed in Group III) in their compounds. The similarities among these elements and their compounds are so profound that they were earlier mistaken to be a single element. Elaborate processes of fractionation could, however, separate them. These are followed by actinium (Ac), together with 14 other elements from thorium (Th) to Lawrencium (Lw), generally called the **actinide elements** or **actinons.** These are all radio-active elements and many of them (transuranic elements) do not occur in nature, but have been prepared artificially. The electronic structures of the actinons are similar to the lanthanons, except that the inner 5*f* shell is gradually filled up by electrons in these cases as the atomic number of the elements increases.



Of the elements of the 3rd main group, boron and aluminium are very abundant, but the other three (Ga, In, Tl) are rare. Although Ga, In and Tl are fairly widely distributed in the earth's crust, they occur almost invariably in minimal concentrations, as isomorphous replacements in certain minerals of the other elements. They are thus rare elements—gallium and indium, indeed, are exceedingly rare; they were all discovered by spectroscopic methods.

In our discussion here, we will deal with only **boron** and **aluminium.**

### BORON AND ALUMINIUM.

Although boron and aluminium are the two *typical* elements of Group III of the Periodic Table, boron has very little resemblances in properties with aluminium or its congeners, *viz.* Ga, In and Tl. The contrasts are rather more conspicuous, and boron resembles very closely the element silicon in the next group (Group IV),—a vivid manifestation of the *diagonal relationship* generally exhibited by the typical elements. Boron lies in the border-line between metals and non-metals, and definitely behaves as a non-metal, while aluminium is a typical metal.* The atoms of both the elements have 3 electrons in their outermost quantum shell, and these electrons actually function as the valence-electrons, so that the typical group-valency of both the elements is 3. [In some of its volatile hydrides, however, boron appears to exhibit anomalous valency.] Some important physical data of the two elements are given in the Table below:

| Property | Boron | Aluminium |
|---|---|---|
| Atomic Number | 5 | 13 |
| Atomic weight | 10.82 | 26.97 |
| Electronic configuration | $1s^2\ 2s^2\ 2p^1$ | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ |
| Density at 20°C | 2.34 | 2.7 |
| Atomic radius (Å) | 0.2 | 0.5 |
| Valency | 3 | 3 |
| Melting point (°C) | 2300 | 659.8 |
| Boiling point (°C) | 2550 | 2270 |
| Electronegativity (Pauling) | 2.0 | 1.5 |
| Standard potential (E°), volts ($M \rightleftharpoons M^{+3}+3e$) | 0.73 ($H_3BO_3$) | 1.67 |

As a non-metal, boron is not a conductor of heat or electricity; but, being a typical metal, aluminium is a good conductor of heat and electricity. Boron has a very high melting point (2300°C), but aluminium melts at a comparatively much lower temperature (659.8°C). Boron does not dissolve in HCl, but aluminium readily dissolves in this acid to form aluminium chloride and evolving hydrogen. Aluminium dissolves in strong aqueous solutions of alkalis, with the evolution of hydrogen ; boron also dissolves on fusing with alkalis to evolve hydrogen. Boron has two allotropes, but aluminium does not exhibit allotropy. The small atomic volumes of these two elements and the triple charge on their ions indicate that the compounds of boron and aluminium should tend to be covalent in nature. That it is often true, is revealed by the properties of many of their compounds. [It should be noted that the compounds $B_2O_3$, BN, $BCl_3$ of boron, although similar in composition to the corresponding compounds $Al_2O_3$, AlN and $AlCl_3$ of aluminium, their properties are quite different.] But, the compounds of boron are mainly covalent, but some of the aluminium compounds are covalent in the gaseous state, but they generally ionise in aqueous solution. The common compounds of boron are derivatives of very weak, covalent boric acid, $B(OH)_3$. The maximum covalency of boron is 4 (as in $KBF_4$, potassium fluoborate). Aluminium also exhibits a covalency 4 in the voltaile dimeric aluminium chloride, ($Al_2Cl_6$), as well as in the coordination complexes such as $Na[AlCl_4]$, $[AlCl_3(NH_3)]$, $[AlCl_3(PH_3)]$ *etc.* But, it can also act as hexacovalent ion, as in $Na_3[AlF_6]$, $[Al(NH_3)_6]Cl_3$ *etc.*

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*The penultimate shell of the boron atom contains only 2 electrons ($1s^2$), while that of the aluminium atom contains 8 electrons ($2s^2\ 2p^6$). This difference in the electronic structure of the two atoms has been suggested as the cause of the difference in the properties of the two elements.

Boron forms many volatile, inflammable and hydrolysable hydrides, whereas aluminium forms only a solid polymeric hydride of uncertain structure. Boron trioxide ($B_2O_3$) is weakly acidic and aluminium trioxide ($Al_2O_3$) is weakly basic, but both are amphoteric. Boron trichloride ($BCl_3$) is a purely covalent compound and a gaseous substance at ordinary temperature (it can be liquefied at very low temperature), but aluminium chloride ($AlCl_3$) is a volatile solid, easily sublimable and is dimeric in the gaseous phase (and hence covalent). These two chlorides can be prepared from the corresponding trioxides ($Al_2O_3$ and $B_2O_3$) by heating with powdered coke in a current of dry $Cl_2$ gas :

$$Al_2O_3+3C+3Cl_2=2AlCl_3+3CO.$$

$$B_2O_3+3C+3Cl_2=2BCl_3+3CO.$$

Boron trichloride is readily hydrolysed to give boric acid, $B(OH)_3$, but aluminium chloride is partially hydrolysed in water to give $Al(OH)_3$. Both boron and aluminium form oxy-salts like sulphate and phosphate, but carbonates are not known. Sulphides of both the elements are completely decomposed by water. Both aluminium and boron form nitrides which react with water to form ammonia. Complex salts of both boron and aluminium are known, in which the elements are present both in the cation or anion. Organometallic compounds are also formed by both boron and aluminium. The alkoxide of aluminium, $Al(OR)_3$ is similar to borate ester, $B(OR)_3$.

**Boron and Silicon Compared :**

Although boron occurs in Group III and silicon in Group IV of the Periodic Table, the two elements resemble each other very closely. Both of them are non-metals and are bad conductors of heat and electricity. The two elements exhibit allotropy, forming amorphous and crystalline varieties, and the allotropic modifications are comparable in properties. Both amorphous boron and amorphous silicon are prepared by similar method, *viz.* by reducing potassium fluoborate and potassium fluosilicate by heating with metallic sodium, or by heating the oxides $B_2O_3$ and $SiO_2$ with magnesium powder. Crystalline boron and crystalline silicon are alike in hardness. Melting points of both B and Si are high, but their densities and atomic volumes are low. Both the elements form covalent compounds.

On burning in air, boron forms $B_2O_3$ and BN (boron nitride), but silicon forms only $SiO_2$ when burnt in air. $B_2O_3$ and $SiO_2$ are similar in their acidic nature, as is shown by their ability to react with metallic oxides to form borates and silicates respectively. Both of them readily form glassy mass which is difficult to crystallise. Both boron and silicon dissolve, when fused with alkalis, to form borates and silicates respectively, evolving hydrogen. Boron dissolves in oxidising acids like $HNO_3$, but not in HF ; silicon dissolves both in HF and $HNO_3$. Boron and silicon combine on heating with metals to form borides and silicides respectively, which are very similar in nature. The two elements also react with carbon at high temperatures to form analogous carbides. The borides and silicides are very hard but brittle substances. The hydrides of both boron and silicon are volatile, spontaneously inflammable and readily hydrolysed. [Boron, however, forms a number of hydrides which are structurally unique, with unusual stoichiometries, configurations and bonding, all arising out of their electron-deficient nature.] Boron and silicon form gaseous fluorides $BF_3$ and $SiF_4$ respectively, which are hydrolysed by water :

$4BF_3+3H_2O=3HBF_4+B(OH)_3; 3SiF_4+4H_2O=2H_2SiF_6+Si(OH)_4$.

The chlorides, $BCl_3$ and $SiCl_4$, are formed by direct union of chlorine with heated boron and silicon respectively, or by the action of $Cl_2$

on a heated mixture of carbon and $B_2O_3$ and $SiO_2$ respectively. Both are readily hydrolysed to give boric acid and silicic acid respectively. The similarity and complexity of the boric and silicic acids are notable. Salts of some of these acids, such as the metaborates and pyroxene silicates, containing the linear units $(BO_2)_x$ and $(SiO_3)_x$ respectively, are structurally similar.

## BORON

*Symbol* : B ; *Atomic No.*=5 ; *Atomic weight*=10.82

*Electronic configuration* : $1s^2\ 2s^2\ 2p^1$

Although the early history of boron and its compounds is somewhat obscure, borax appears to be the first mineral of the element that was traded in the ancient world. The Babylonians in 2000 B.C. imported it from the Far East for use in the working and welding of gold. It was also used by the ancient Egyptians and Greeks to prepare hard glass. Borax glazes were known by 300 A.D. At this time, the main source of the material was at Tibet. Marco Polo brought the first authentic specimen of borax from Mongolia to Europe in the 13th century, and it was called *tincal* from its Sanskrit name *tinaca*. By the middle of the 16th century, borax was widely used throughout Europe as a flux. G. Homberg (1702) obtained boric acid by treating borax with ferrous sulphate, and the product was named *Sal Sedativum*, on account of its medicinal properties. L. Lemery (1728) and C. J. Geoffroy (1732) obtained boric acid by heating borax with mineral acids, and T. Baron (1747) showed that borax was a compound of boric acid and sodium metal. Impure boron was first isolated simultaneously by Gay Lussac, Thenard and Davy (1808). Moissan (1892) obtained about 98.3% pure boron by the reduction of boric acid with magnesium metal, followed by further purification. High purity boron was first made by Weintraub (1909) by arc melting of Moissan's boron and also by passing a mixture of boron trichloride and hydrogen through an arc between water-cooled copper electrodes.

**OCCURRENCE** : Boron occurs as a trace element in most soils ; it is present in sea-water to the extent of a few parts per million and is estimated to constitute about 10 parts per million of the earth's crust. Although boron is thus widespread in nature, commercially valuable deposits of boron have been found only in a few places like Italy, U.S.A. (California), U.S.S.R., Tibet and Turkey. California, where the world's largest single source of boron occurs (at Kramer, as borates), has for many years been the world's biggest producer of boron ores. Most of the major deposits of boron have been found in areas of former volcanic activity and can be associated with the water of former hot springs. The most important and economic minerals of boron are : (1) **Borax** ($Na_2B_4O_7.10H_2O$) and **Kernite**

($Na_2B_4O_7.4H_2O$), (2) **Colemanite** ($Ca_2B_6O_{11}.5H_2O$), (3) **Ulexite** [$Na_2Ca_2(B_4O_7)_3.18H_2O$] and (4) **Boracite** ($2Mg_3B_8O_{15}.MgCl_2$).

**PREPARATION OF BORON** : Boron exists in two allotropic modifications, *viz.* amorphous boron and crystalline boron. Amorphous boron is prepared as a brown powder by the reduction of boron trioxide or potassium fluoborate ($KBF_4$) by means of metallic sodium (or potassium or magnesium) at red-heat. Impurities present in the product are generally removed to a large extent by boiling first with dil. HCl and then treating it with hydrofluoric acid. By this procedure, about 98.3% pure boron can be obtained : $B_2O_3+6Na=2B+3Na_2O$ ; $B_2O_3+3Mg=2B+3MgO$ ; $KBF_4+3K=B+4KF$ ; $2KBF_4+3Mg=2B+2KF+3MgF_2$.

The manufacture of amorphous boron is also carried out by the the reduction of $B_2O_3$ by metallic magnesium at red-heat. The $B_2O_3$, required for the purpose, is prepared from the minerals borax or colemanite. When colemanite is used, it is first converted into borax by boiling with sodium carbonate solution :

$$2Ca_2B_6O_{11}+3Na_2CO_3+H_2O=3Na_2B_4O_7+3CaCO_3+Ca(OH)_2.$$

Borax is then treated with conc. HCl, when sparingly soluble boric acid slowly separates out :

$$Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3.$$

Boric acid is strongly heated to obtain boron trioxide :

$$2H_3BO_3=B_2O_3+3H_2O.$$

Boron trioxide is then reduced to boron by heating with metallic magnesium :

$$B_2O_3+3Mg=2B+3MgO.$$

Crystalline boron is prepared as a black material by the thermal decomposition (1200°C) of boron trichloride or boron tribromide vapours in contact with tungsten or tantalum filament (Van Arkel and De Boer method), or by the decomposition of boron trichloride by high frequency sparks between tungsten or copper electrodes, in presence of hydrogen (Hackspill method). Crystalline boron can also be prepared from amorphous boron, by fusion and crystallisation, or by melting it with aluminium, or by reducing boron trioxide with aluminium. In the last two cases, however, the element is associated with aluminium in the form of a compound, $AlB_{12}$.

**PROPERTIES** : Amorphous boron is a tasteless, odourless brown powder of density 1.73, but the pure crystalline boron is very hard and blackish-grey in colour, with a density of 2.34. The melting point of both the varieties of boron is very high (2300°C). Crystalline boron is very resistant to chemical action ; even oxidising agents, hot and conc. $HNO_3$, $H_2SO_4$, HCl or HF *etc.* have no effect on it. But, it is oxidised to borate on fusing with sodium peroxide, or a mixture of $Na_2CO_3$ and $KNO_3$. Amorphous boron, on the other hand, is much more reactive. When heated in air at about 700°C, it burns with a reddish flame to form boron trioxide and some boron nitride. It directly reacts, on heating, with many metals and some non-metals like halogens, carbon and sulphur, to form binary compounds like metallic borides, boron trihalides, boron carbide and boron sulphide. The reaction with nitrogen takes place from 900°C upwards. On boiling with conc. $HNO_3$ or aqua regia, it is oxidised to boric acid, and on boiling with alkalis, alkali borates are formed, with the liberation of hydrogen : $B+3HNO_3=H_3BO_3+3NO_2$ ; $2B+6KOH=2K_3BO_3+3H_2$. It is oxidised by steam at red-heat, liberating hydrogen : $2B+3H_2O=B_2O_3+3H_2$. Under similar condition of temperature, nitric oxide reacts with boron to give boron trioxide and boron nitride : $5B+3NO=B_2O_3+3BN$. It can displace metals from their oxides, sulphides or chlorides, when heated.

**USES** : Boron is sometimes used as a de-oxidiser for casting copper. *Ferro-boron* (20% B, 80% Fe) is often used in steel industry for hardening speical steels. Compounds of boron, such as boric acid, borax, alkali perborates have extensive applications.

## COMPOUNDS OF BORON.

**Boron Hydrides** : When metallic magnesium is heated with boron trioxide, magnesium boride is formed. Treatment of magnesium boride with dil. HCl liberates a gas, consisting mostly of hydrogen, admixed with some other unpleasant-smelling gas. Alfred Stock and his co-workers (1912-1936) made elaborate studies on these gaseous products and characterised in the mixture a number of boron hydrides or boranes with unique stoichiometries and structures. The following hydrides of boron were prepared and studied by Stock and co-workers :

| Compound | m.p. (°C) | b.p. (°C) |
|---|---|---|
| $B_2H_6$ (Diborane) | −160.5 | −92.5 |
| $B_4H_{10}$ (Tetraborane) | −120 | 18 |
| $B_5H_9$ (Pentaborane) | −46.6 | 48 |
| $B_5H_{11}$ (Pentaborane-11) | −123 | 63 |
| $B_6H_{12}$ (Hexaborane) | −65 | 0 (at 7 mm.) |
| $B_{10}H_{14}$ (Decaborane) | 99.7 | 213 |

Only recently, two other boranes, $B_9H_{15}$ and $B_{10}H_{16}$ have been characterised.

**Preparation :** (i) Stock's original method of preparing boranes consists in dropping pieces of magnesium boride into a 10% solution of hydrochloric acid at 50°C, contained in a vessel, in which a stream of hydrogen gas was passed. (This is essential, as boranes react with oxygen of the air). Better yield of boranes is obtained by using 8N phosphoric acid at 70°C. The evolved gas (mainly $H_2$, with small quantities of boranes, silanes or silicon hydrides, phosphine *etc.*) is cooled by liquid air, when the hydrides are condensed to a liquid. The individual boranes are obtained from this liquid by repeated fractionation. The yield of boranes by this method is very poor ; 5 gms. magnesium boride give only about 1 ml. of the gaseous hydrides. Diborane, $B_2H_6$, is not practically formed in this method, the main product being tetraborane, $B_4H_{10}$, for which this original method of Stock is used now-a-days.

(ii) Better yields, particularly of diborane, are obtained by submitting a mixture of boron trichloride (or tribromide) and excess of hydrogen to the silent electric discharge at a pressure of less than 10 mm. The primary product is a monohalogen diborane, which rapidly disproportionates into diborane and boron trihalide :

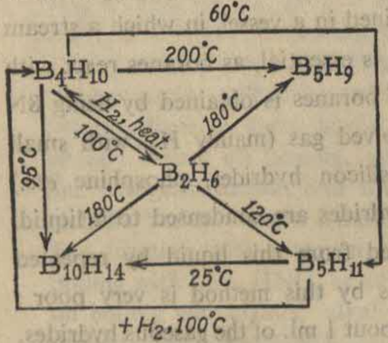
$$2BCl_3+5H_2=B_2H_5Cl+5HCl \; ; \; 6B_2H_5Cl=5B_2H_6+2BCl_3.$$

(iii) The best method of preparation of $B_2H_6$ is, however, the reduction of boron trichloride or of boron trifluoride etherate by lithium aluminium hydride (or sodium borohydride, $NaBH_4$), or lithium hydride. The yield of diborane by this method is almost quantitative : $4BCl_3+3LiAlH_4=3LiCl+3AlCl_3+2B_2H_6$.

(iv) Tetraborane, on pyrolysis, breaks up into diborane and higher boranes. The amount of the higher boranes depends on the experimental conditions, particularly temperature, under which the pyrolysis is carried out. By suitable choice of conditions, the method can be used to prepare $B_5H_9$, $B_5H_{11}$ and $B_{10}H_{14}$ (but $B_6H_{10}$ is not formed by this method).

(v) Tetraborane may be obtained by the action of sodium on chloro- or bromodiborane : $2B_2H_5Cl+2Na=B_4H_{10}+2NaCl$.

The thermal inter-conversion of boranes are shown in the figure :

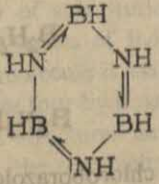


**General properties of boranes** : Diborane, if pure, does not inflame spontaneously when mixed with air or oxygen, but the other boranes do. They are all hydrolysed by water with the evolution of hydrogen and forming ultimately boric acid, $H_3BO_3$ ; but, the ease with which such hydrolysis takes place differs greatly in the cases of different boranes. Without further discussion of the properties of the boranes in general, we will describe below the properties of diborane, which are considered to be representative of those of the other boron hydrides.

**Properties of diborane** : This hydride of boron has been more fully studied than the other hydrides. Diborane is a colourless gas, boiling at −92.5°C, and at very low temperatures, it can be frozen to a solid which melts at −165.5°C. At red-heat, it decomposes to boron and hydrogen. It is not spontaneously inflammable at ordinary temperatures, but reacts with oxygen to form a dark-coloured product of indefinite composition. It is very readily hydrolysed with water, the ultimate products of hydrolysis being boric acid and hydrogen : $B_2H_6+6H_2O=2H_3BO_3+6H_2$. Reaction with methyl alcohol gives the corresponding ester of boric acid : $B_2H_6+6CH_3OH=2B(OCH_3)_3+6H_2$. With cold concentrated alkali solutions, diborane forms alkali hypoborate : $B_2H_6+2KOH=2KOBH_3+H_2$.

[Alkali hypoborates are very powerful reducing agents which liberate hydrogen from water, precipitate metals like Ag, Hg, As, Sb, Bi *etc.* from solutions of their salts (but with solutions of nickel salts, nickel boride, $Ni_2B$, is curiously formed).]

Diborane reacts violently with chlorine to give boron trichloride and hydrogen : $B_2H_6+6Cl_2=2BCl_3+6HCl$. The reaction with bromine is similar, but is less vigorous and controllable. Iodine has little reaction with $B_2H_6$. Hydrochloric acid reacts very slowly with diborane to form chlorodiborane : $B_2H_6+HCl=B_2H_5Cl+H_2$. HBr and HI react with diborane at some elevated temperatures and in presence of catalyst, to form bromodiborane and iododiborane respectively, but both these compounds pass into diborane and boron tribromide (or triiodide) on keeping : $6BH_3.BH_2Br=5B_2H_6+2BBr_3$. When shaken with sodium, potassium or calcium amalgams, diborane forms salt-like adducts, which have been formulated as $2Na^+(B_2H_6)^{=}$. The behaviour of diborane with ammonia is curious. At or below room temperature, ammonia reacts with diborane to give an addition-product with the composition, $B_2H_6 . 2NH_3$ (a colourless solid). This, on heating to 200°C, forms a liquid (b.p. 55°C) which has a molecular composition $B_3N_3H_6$ : $B_2H_6+2NH_3=B_2H_6.2NH_3$ ; $3(B_2H_6.2NH_3)=2B_3N_3H_6+12H_2$. This product has been shown to be a cyclic compound, containing a six-membered ring, in which boron atoms and nitrogen atoms alternate. This heterocyclic boron compound has been named **Borazole** or **inorganic benzene.** Borazole is more easily prepared (35% yield) by the reaction between lithium borohydride and ammonium chloride : $3LiBH_4+3NH_4Cl=B_3N_3H_6+9H_2+3LiCl$. Borazole is a colourless liquid with aromatic smell and solvent properties (hence the name **inorganic benzene**), but is more reactive than benzene.



Borazole

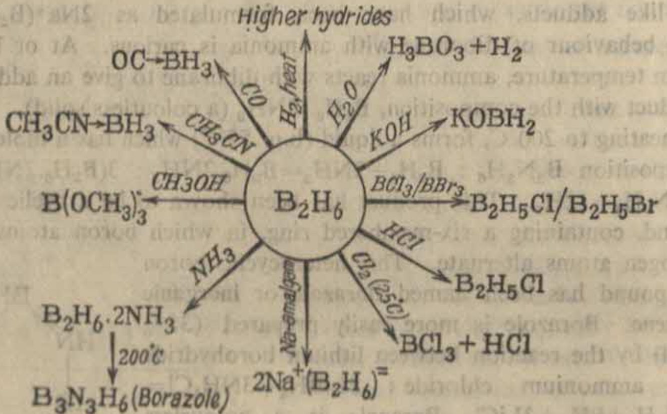
[This structure of borazole agrees with its infra-red and Raman spectra, and with its ability to form two series of trimethyl derivatives, *viz.* the tri-N-methyl borazole, where the methyl groups are attached to the N-atoms of the ring (and gives methyl amine and boric acid on hydrolysis) and tri-B-methyl borazole, where the methyl groups are attached to the boron atoms (and gives ammonia and boric acid on hydrolysis.]

In many of its reactions, diborane appears to act through the formation of an intermediate, $BH_3$ (borine), although this has never been isolated. Thus, diborane reacts with donor molecules to form compounds containing coordination bond :

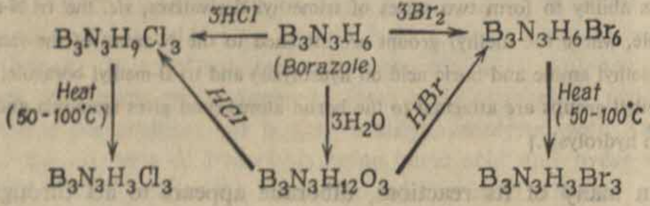
$B_2H_6+2CO=2\ OC\rightarrow BH_3$(Borine carbonyl)
$B_2H_6+2CH_3CN=2\ CH_3CN\rightarrow BH_3$ (Broine acetonitrile adduct)
$B_2H_6+2(CH_3)_3N=2(CH_3)_3N\rightarrow BH_3$(Borine trimethylamine adduct)
$B_2H_6+2PF_3=2PF_3\rightarrow BH_3$ (Borine trifluorophosphine adduct.)

The reactions of diborane are summarized in the next page.

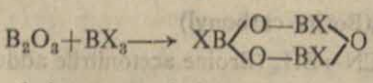
**Reactions of borazole :** The main difference of borazole from benzene is its susceptibility to hydrolysis. It is hydrolysed on boiling with water to give boric acid, ammonia and hydrogen : $B_3N_3H_6+9H_2O=3H_3BO_3+3NH_3+3H_2$. On boiling with alkali solutions also, similar rupture of the borazole ring takes place. But, like the benzene ring, the borazole ring is also a resonating structure and B:B:B-tri-



chloroborazole has similar structure as 1:3:5-trichlorobenzene. With HCl, $Br_2$ and $H_2O$, borazole first forms addition-products ; but, on heating (50-100°C), the former two products give the halogen-substituted borazoles. These reactions are shown below :



**Boroxoles** : These are also six-membered heterocyclic boron compounds, in which boron atoms alternate with oxygen atoms. These are formed by the general reaction :



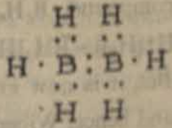
$$B_2O_3+BX_3 \longrightarrow XB\begin{matrix}\diagup O-BX \diagdown \\ \diagdown O-BX \diagup\end{matrix}O$$

(X=halogens, methyl or methoxyl groups)

**Structures of Boranes** : The boranes belong to a class of *electron-deficient* compounds. In their molecules, there are more potentially bonding and stable orbitals available than there are electron-pairs to form covalent bonds. Their stoichiometries are quite unusual, and these cannot be explained by normal ideas of bond formation. As a result, their structures are of great interest and present a problem in the domain of structural inorganic chemistry. We will discuss here, in details, the structure of diborane, taking it as the representative of all the boranes.

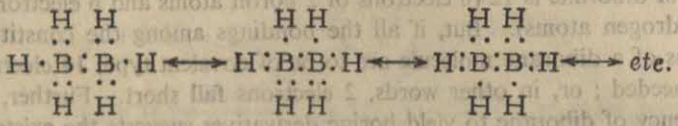
**Structure of Diborane** : The molecular formula of diborane is $B_2H_6$ and its chemical and physical behaviours point to its covalent nature. The total number of bonding electrons contained in a molecule of diborane is 12 (6 electrons of 2 boron atoms and 6 electrons of 6 hydrogen atoms). But, if all the bondings among the constituent atoms of a diborane molecule are to be of covalent type, 14 electrons are needed ; or, in other words, 2 electrons fall short. Further, the tendency of diborane to yield borine derivatives suggests the existence of two $BH_3$ entities in a molecule of $B_2H_6$, or the formation of $BH_3$ during the course of its reaction. The impossibility of substitution of alkyl groups for more than four of the hydrogen atoms of $B_2H_6$ also suggests that two hydrogen atoms in a diborane molecule is associated with it in a manner different from that of the other four hydrogen atoms. To account for all these behaviours, various structures have been suggested from time to time for diborane. But, the real picture of the structure could only be corroborated by the physical methods of structure determination, rather by the chemical characteristics of the compound. Of the various structures proposed for diborane, the following three types merit discussion : (i) *ethane-like* structure, (ii) ionic structure and (iii) *hydrogen-bridge* structure.

(i) The composition of diborane ($B_2H_6$) and the superficial analogy of the formation of decaborane by the reaction of monohalodiborane with metallic sodium (*cf.* Wurtz reaction), obviously suggest an ethane-like structure of diborane, and this was originated from Sidgwick's suggestion (1927) that two of the hydrogen atoms in diborane are held by one-electron bonds, with an electron-pair bond between the two boron atoms as shown in the figure.

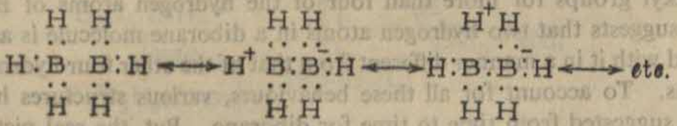


$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{H} & \cdot & \mathrm{B} & : & \mathrm{B} & \cdot & \mathrm{H} \\ & & \cdot\cdot & & \cdot\cdot & & \\ & & \cdot\mathrm{H} & & \mathrm{H} & & \end{array}$$

The nearly equal electronegativities of boron and hydrogen is favourable for the formation of one-electron bond between the two atoms, and the electron diffraction photograph of $B_2H_6$ is similar to that of ethane. But, a serious objection to such a structure arises due to the fact that diborane is actually diamagnetic, whereas the compound with one-electron bond should exhibit paramagnetism. Pauling suggested that the diborane molecule is the resonance-hybrid of six structures, in which the one-electron bond takes different positions. Further resonance may also involve structures containing zero-electron bond (Lewis), so that six electron-pair bonds resonate between seven positions (including between two B atoms), conferring on each of the seven bonds 6/7 single-bond and 1/7 no-bond character, as shown below :

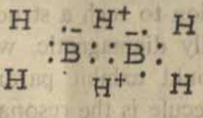


Pauling's structure

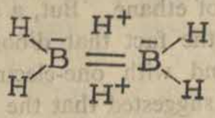


Lewis' structure

(ii) **Ionic structure** : Electrovalently held hydrogen in the molecule of diborane was invoked by Wiberg (1936), inspite of the apparent absence of electrovalent properties of the compound. Such an idea probably had its origin from the very faint acidic character of diborane and its reaction with ammonia to produce the additive-compound, $B_2H_6$. $2NH_3$. Diborane was, therefore, represented as $H^+[H_2\bar{B}=\bar{B}H_2]H^+$, and the ammonia-adduct as $NH_4^+[H_2\bar{B}=\bar{B}H_2]NH_4^+$. But, it is now known that the compound contains B—N—B linkages and hence, Wiberg's representation is not tenable. A later modification (Pitzer, 1945) of Wiberg's structure was based on the assumption that the electrons forming the double bond still possessed some unused valency properties and could thus bind protons to form the so-called *protonated double bond* as in,

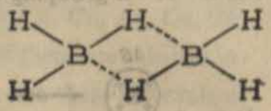


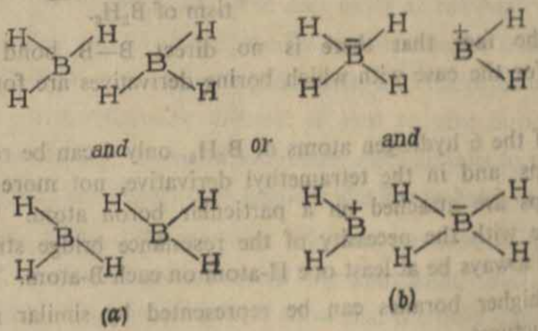
or



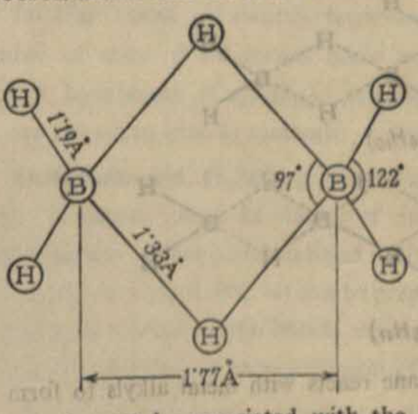
Although this may amount to an ionic structure, it is better consideraed as a variation of hydrogen-bridge concept of the structure of diborane as stated overleaf.

(iii) *Hydrogen-bridge structure* : This is the most attractive theory regarding the structure of diborane (or the other boranes), and it postulates *resonance bridge* between the boron atoms (Dilthey and Core, 1921-27). According to this view, diborane is structurally represented in the simple form as shown, where the terminal B—H bonds are normal electron-pair bonds and the central B—H bonds result from resonance between either covalent structures of type (*a*) or ionic srtuctures of type (*b*) :

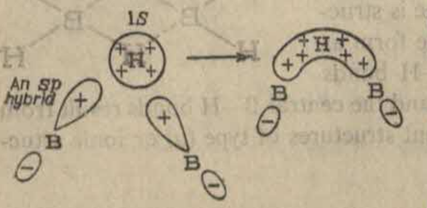




Such structures have been supported by electron diffraction and infra-red spectral measurements. It has been shown that the two boron atoms and the four terminal hydrogen atoms are coplanar and the two bridging hydrogen atoms lie symmetrically above and below this plane. The two bridging H-atoms restrict rotation about the two boron atoms, which is supported by the measurement of specific heat. The terminal B—H bonds are normal electron-pair covalent bonds, as is revealed by their bond lengths (1.19Å). Hence, the electron-deficiency in the compound must be associated with the bridging groups. The bridging bonds are indeed abnormal, as they involve only one electron from each boron atom and one from each H-atom, making a total of 4



electrons. One $sp^2$-hybrid orbital from each boron atom overlaps with 1*s* orbital of the H-atom, resulting in a delocalised orbital covering one B—H—B grouping of the bridge, as shown below :



The resonance bridge structures are corroborated by the facts that :

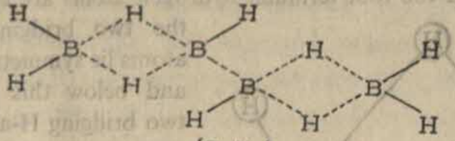
(a) All resonating forms whether of type (*a*) or (*b*) contain only paired electrons accounting for the diamagnetism of $B_2H_6$.

(b) The fact that there is no direct B—B bond in $B_2H_6$ accounts for the ease with which borine derivatives are formed from $B_2H_6$.

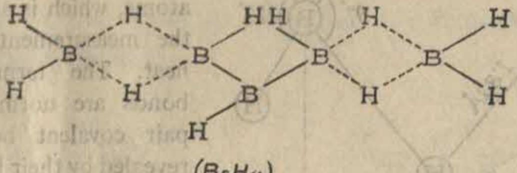
(c) Of the 6 hydrogen atoms of $B_2H_6$, only 4 can be replaced by $CH_3$-groups and in the tetramethyl derivative, not more than two $CH_3$-groups are attached on a particular boron atom. This is in accordance with the necessity of the resonance bridge structure as there shall always be at least one H-atom on each B-atom.

The higher boranes can be represented by similar resonance-bridge structures.

Cyclic structures (as shown below for $B_4H_{10}$ and $B_5H_{11}$) have also been assigned to the higher boranes :



($B_4H_{10}$)



($B_5H_{11}$)

**Metal Borohydrides :** Diborane reacts with metal alkyls to form *metal borohydrides* or *boranates* :

$$Al(CH_3)_3 + 2B_2H_6 = B(CH_3)_3 + \underset{\text{Aluminium borohydride}}{Al(BH_4)_3}$$

Salt-like metal hydrides also react with diborane to give the corresponding metal borohydrides : $2NaH+B_2H_6=2NaBH_4$.

The borohydrides of Li Na, K, Be, Mg, Zn, Cd, Cu, Ag, Ga, Ti, Zr, Hf, Th and U have been prepared. Most of them are salt-like in character, but a few are volatile, with properties like those of covalent compounds.

**Boron Trioxide, $B_2O_3$,** is formed as a colourless, brittle, vitreous, hygroscopic mass, on burning boron in oxygen, or by the ignition of boric acid. It has a density of 1.844 and melts at red-heat without any decomposition. It is not reduced by carbon even at white heat. Boron trioxide is a non-conductor of electricity and dissolves in water with evolution of considerable amount of heat to give boric acid : $B_2O_3+3H_2O=2H_3BO_3$. It reacts with many metallic salts to produce beads of characteristic colours (See below under **Borax-bead Test**).

**Boric Acid** : Three different boric acids are reported in chemical literature. These are all derived from the anhydride, $B_2O_3$. But, the phase studies of $B_2O_3$-$H_2O$ system show that the only stable acids are the metaboric acid, $HBO_2$ and the orthoboric acid, $H_3BO_3$. The tetraboric acid or pyroboric acid, $H_2B_4O_7$, although often reported in older literature, has practically no stable existence, although its salt, the familiar borax or sodium tetraborate is very stable. A large number of salts of condensed boric acids or polyborates, such as calcium hexaborate ($Ca_2B_6O_{11}$), magnesium octaborate ($Mg_3B_8O_{15}$) *etc.* are known to exist in minerals.

**Orthoboric acid, $H_3BO_3$,** is the most important among the boric acids. It occurs native in waters of many hot springs, in volcanic areas (Tuscany in Italy) and in dried up lagoons (in Tibet). In traces, it is present in many fruits. It can be prepared by the action of dil. HCl or $H_2SO_4$ on a solution of a borate, especially borax. The precipitated boric acid is purified by recrystallisation from hot water.

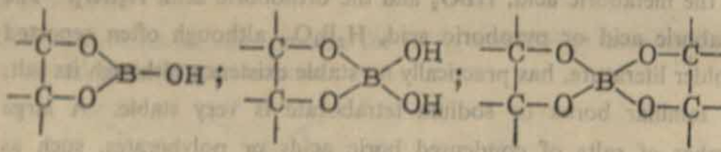
Boric acid is generally manufactured from the mineral colemanite ($Ca_2B_6O_{11} . 5H_2O$). The finely powdered mineral is dissolved in boiling water and $SO_2$ gas is passed through the hot solution. As a result, boric acid and calcium bisulphite are formed in solution. On cooling, boric acid separates out, leaving calcium bisulphite in solution. It is filtered, washed with cold water and dried in air.

$$Ca_2B_6O_{11}+4SO_2+11H_2O=2Ca(HSO_3)_2+6H_3BO_3.$$

Boric acid forms white, transparent, flaky leaflets (density=1.46). It is quite soluble in water and the solubility rises greatly with the rise of temperature [solubility : at 0°C=19.47 gms./litre ; at boiling point of saturated solution (102°C)=291.2 gms./litre]. The acid is volatile with steam. When heated, it decomposes to metaboric acid and then through pyroboric acid to boron trioxide :

$$H_3BO_3 \xrightarrow{175°C} [HBO_2 \longrightarrow H_2B_4O_7] \xrightarrow[\text{(fused)}]{\text{red heat}} B_2O_3.$$

It is a very weak acid and as such, the soluble alkali metal borates are extensively hydrolysed in solution, giving an alkaline reaction. But, the addition of polyhydroxy compounds, such as mannitol or glycerol, enhances its strength by converting it to a strong monobasic acid. Only polyhydric alcohols with hydroxy groups on the adjacent



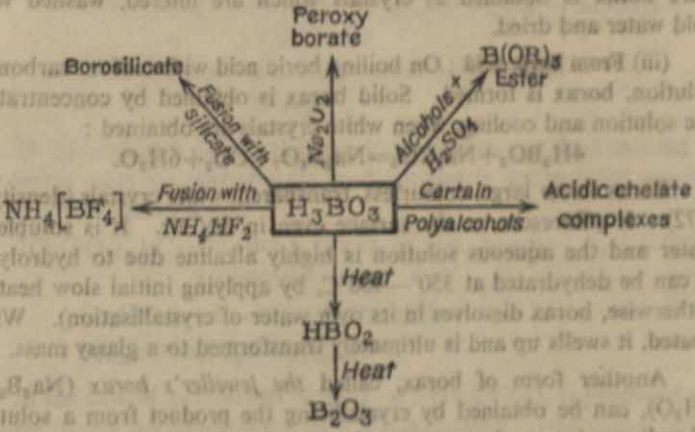
carbon atoms *cis* to each other are effective in enhancing the strength of boric acid. The effect is due to the formation of chelate complexes of the above types and is of considerable analytical importance. Boric acid reacts with methyl alcohol (or ethyl alcohol) in presence of conc. $H_2SO_4$ to form ester, *viz.* methyl borate (or ethyl borate) which is a volatile liquid that burns with a green-edged flame :

$$H_3BO_3+3CH_3OH=B(OCH_3)_3+3H_2O.$$

Boric acid reacts with ammonium hydrogen fluoride to give ammonium fluoborate :

$$H_3BO_3+2NH_4HF_2=NH_4[BF_4]+3H_2O+NH_3.$$

Silicate minerals, on fusion with boric acid, form borosilicates, which can be decomposed by HCl. When boric acid is melted with sodium peroxide, sodium peroxyborate is formed. The reactions of boric acid are summarised below :



Boric acid is used in large quantities for the manufacture of borax and also as glazes in enamel industries. In medicine, it is used as a disinfecting powder for wounds, for impregnating surgical dressings and also to prevent excessive perspiration. In candle industries, it is used to stiffen wicks. In certain countries, it is permitted to be used as a preservative for foods. It also finds application in tanning and in pigment manufacture.

**Borax, Sodium tetraborate decahydrate, $Na_2B_4O_7.10H_2O$** : The most important salt of boric acids is borax. It occurs as *tincal* in Tibet, South America, California and Nevada. The tetrahydrate, $Na_2B_4O_7.4H_2O$ (*Kernite*) occurs in large quantities as deposits in California. Many minerals contain complex metallic borates, of which *colemanite* ($2CaO.3B_2O_3$) is largely used for the production of borax.

*Preparation of borax* : (i) **From Colemanite.**—Finely powdered colemanite is boiled with sodium carbonate solution, when calcium carbonate is precipitated. It is filtered off and the filtrate is concentrated, when crystals of borax are formed. These are separated and dried. The mother-liquor contains sodium metaborate ($NaBO_2$), which is converted into borax by passing $CO_2$ through the solution, and thus a further crop of borax is obtained.

$$2CaO.3B_2O_3+2Na_2CO_3=Na_2B_4O_7+2NaBO_2+2CaCO_3\downarrow ;$$
$$4NaBO_2+CO_2=Na_2B_4O_7+Na_2CO_3.$$

(ii) **From Tincal** : The native deposits of tincal are dried crude borax, from which the purer product can be obtained by recrystallising the deposits from hot water. On cooling the hot solution, almost pure borax is obtained as crystals which are filtered, washed with cold water and dried.

(iii) **From boric acid** : On boiling boric acid with sodium carbonate solution, borax is formed. Solid borax is obtained by concentrating the solution and cooling, when white crystals are obtained :

$$4H_3BO_3+Na_2CO_3=Na_2B_4O_7+CO_2+6H_2O.$$

Borax forms large, colourless, transparent white crystals (density= 1.72). It effloresces on the surface even in dry air. It is soluble in water and the aqueous solution is highly alkaline due to hydrolysis. It can be dehydrated at 350°—400°C, by applying initial slow heating (otherwise, borax dissolves in its own water of crystallisation). When heated, it swells up and is ultimately transformed to a glassy mass.

Another form of borax, called *the jeweller's borax* ($Na_2B_4O_7.5H_2O$), can be obtained by crystallising the product from a solution of ordinary borax above 60°C. It is harder than ordinary borax and does not effloresce. It has a density of 1.81.

Borax is widely used in the preparation of glazes for procelain, earthenware and enamelware. It is also used for preparing a special type of glass (borosilicate glass) and optical glasses. Borax is used as a flux in welding and soldering and also in laundering and as a preservative. In chemical laboratories, borax is used for 'borax bead tests', as a volumetric standard and for the preparation of buffer solutions.

The *borax-bead test* consists in heating a minute amount of the sample in a borax-bead (made on a loop of a platinum wire) in the oxidising and the reducing flames of the bunsen burner separately. The colour developed in the bead is observed.

Borax, on heating, first swells up and then melts to form a colourless transparent mass. In this process, borax decomposes into sodium metaborate ($NaBO_2$) and boron trioxide ($B_2O_3$), and the transparent borax bead is actually made up of these two compounds.

When a metallic salt is heated on the borax-bead, it decomposes to the metallic oxide. In the oxidising flame, the higher oxide of the metal is formed, while in the reducing flame, the lower oxide of the metal is formed. These oxides then react with $NaBO_2$ and $B_2O_3$ to form the meta-borate and ortho-borate of the corresponding metals. The colour of the bead is due to the colour of the metaborates (or ortho-borates) of the metals. Thus, with $CuCO_3$, the following reactions occur in the oxidising flame :

$$CuCO_3 = CuO + CO_2$$

$$CuO + NaBO_2 = NaCuBO_3 \text{ (Sodium copper ortho-borate)}$$
(light blue)

$$CuO + B_2O_3 = Cu(BO_2)_2 \text{ (Cupric meta-borate)}$$
(blue)

In the reducing flame, the cupric meta-borate is first reduced to colourless cuprous meta-borate and ultimately to metallic copper, which is dull-red in colour :

$$2Cu(BO_2)_2 + C = Cu_2(BO_2)_2 \text{ (Cuprous meta-borate)} + B_2O_3 + CO.$$
(colourless).

$$Cu_2(BO_2)_2 + C = 2Cu + B_2O_3 + CO$$

$$B_2O_3 + 2NaBO_2 = Na_2B_4O_7.$$

In the case of an iron salt (ferrous or ferric), $Fe_2O_3$ is produced on heating in the oxidising flame, and this ultimately forms *yellow* ferric meta-borate :

$$Fe_2O_3 + 3B_2O_3 = 2Fe(BO_2)_3 \text{ (Ferric meta-borate)}$$
(yellow)

In the reducing flame, ferric meta-borate is reduced to *green* ferrous meta-borate :

$$2\,Fe(BO_2)_3 + C = 2\,Fe(BO_2)_2 \text{ (Ferrous meta-borate)} + B_2O_3 + CO$$
(green)

$$B_2O_3 + 2NaBO_2 = Na_2B_4O_7.$$

Manganese salts form manganic meta-borate (violet) in the oxidising flame, and this is reduced to manganous meta-borate (colourless) in the reducing flame. Chromium and cobalt salts form, in the oxidising flame, green chromic meta-borate, $Cr(BO_2)_3$ and blue cobaltous meta-borate, $Co(BO_2)_2$ (cobaltic meta-borate is not formed). Chromic meta-borate is not reduced in the reducing flame. So, in the cases of chromium and cobalt salts, the same colour of the bead is obtained in both the oxidising and the reducing flames. In the case of nickel salts, the NiO formed in the oxidising flame produces brown $Ni(BO_2)_2$. In the reducing flame, the $Ni(BO_2)_2$ is reduced to metallic nickel and as such, an opaque bead is formed.

**Metaborates** : On heating, boric acid first loses a molecule of water to form metaboric acid, $HBO_2$. It does not exist in solution, as hydration re-forms $H_3BO_3$. In the solid state, the acid and its salts are stable. Two types of metaborates are known—the trimeric cyclic form and the polymeric chain form.

**Peroxyborates and borate peroxyhydrates :**

Peroxyborates (formerly known as *perborates*) are derived from the borates by the replacement of oxygen atom(s) by *peroxo-group* (—O—O—). Many of the so-called perborates are rather addition-compounds of borates with $H_2O_2$, and not true peroxy salts. These are generally prepared by the action of alkali peroxides, or of alkalis containing $H_2O_2$, on borates. Sodium peroxyborate, $NaBO_3$, is prepared by rubbing NaOOH with boric acid. It is decomposed in aqueous solution to give $H_2O_2$, and easily liberates iodine from a neutral solution of potassium iodide.

Of the peroxyhydrates, one of the important compounds is sodium metaborate peroxyhydrate, $NaBO_2.H_2O_2.3H_2O$, which is generally manufactured as a colourless crystalline substance by the anodic oxidation of borax. It is a good oxidising and bleaching agent, and liberates $H_2O_2$ on dissolution in water. It gives up oxygen on heating. It does not liberate iodine from neutral KI solution. It is widely used for preparing disinfecting powders, detergent powders *etc.*

**Boron Halides :** *Boron trifluoride*, $BF_3$, is prepared as a colourless gas with suffocating smell, by heating $B_2O_3$ with $CaF_2$ and conc. $H_2SO_4$: $B_2O_3+3CaF_2+3H_2SO_4=2BF_3+3CaSO_4+3H_2O$. The gas is non-combustible, but it fumes in moist air and is decomposed by water, forming boric acid and fluoboric acid :

$$4BF_3+3H_2O=H_3BO_3+3HBF_4.$$

*Boron trichloride*, $BCl_3$, is obtained as a colourless, mobile, highly refractive liquid (sp. gr.=1.43), by heating boron in chlorine or in dry HCl. It can also be conveniently prepared by passing $Cl_2$ over a heated mixture of $B_2O_3$ and carbon :

$$B_2O_3+3C+3Cl_2=2BCl_3+3CO.$$

Boron trichloride fumes in moist air and is hydrolysed by water :

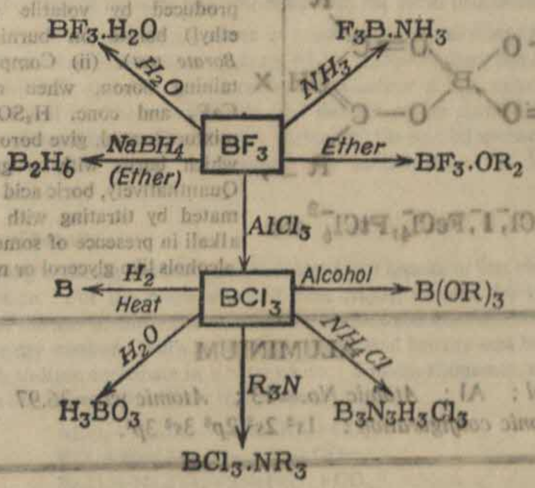
$$BCl_3+3H_2O=H_3BO_3+3HCl.$$

It forms addition compounds with $PCl_3$, $POCl_3$, NOCl *etc.*, and undergoes alcoholysis on reaction with alcohols :

$$BCl_3+3C_2H_5OH=B(OC_2H_5)_3+3HCl.$$

*Boron tribromide*, $BBr_3$, is a colourless, viscous liquid and resembles $BCl_3$ in properties.

A synopsis of important reactions of $BF_3$ and $BCl_3$ is given below :



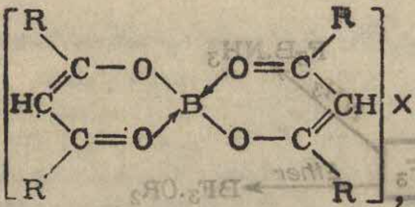
*Boron triiodide*, $BI_3$, is a colourless, hygroscopic solid (m.p. 49°C), and is prepared through the reaction between iodine and sodium borohydride. It is soluble in organic solvents like $CS_2$, $CCl_4$, $C_6H_6$ *etc.* and burns in oxygen with a dazzling flame.

**Boron Sulphide, $B_2S_3$**, is prepared as a vitreous mass by heating boron in sulphur vapour, or by passing $CS_2$-vapours over a heated mixture of $B_2O_3$ and carbon. Its density is 1.55 and it melts at 310°C. It is decomposed by water into $H_3BO_3$ and $H_2S$ : $B_2S_3+6H_2O = 2H_3BO_3+3H_2S$.

**Boron Nitride**, BN, is a white solid of density 2.34, and is obtained by heating boron to white heat in an atmosphere of nitrogen. It has a very high melting point (3000°C under pressure). It is decomposed by steam at red heat, and also on fusion with alkalis, forming ammonia.

**Complexes of Boron** : Boron forms varieties of complex compounds. Boron trihalides, especially $BF_3$, is one of the most avid acceptors and acts as a very strong Lewis acid. It forms adducts with ethers, alcohols, ammonia and amines, phosphines *etc.* The complex tetrahaloborate anions are known, of which the most important is $BF_4^-$. Both the fluoboric acid ($HBF_4$) and its salts are known, in which boron is tetracovalent. The $BF_4^-$ ion has a tetrahedral structure and the tetrafluoborates are isomorphous with perchlorates.

**Cationic boron complexes** are also known, very well-known examples of which are the β-diketonates, with the structures shown below :



where X = $Cl^-, I^-, FeCl_4^-, PtCl_6^{-2}$ etc.

**Tests** : (i) Boric acid or borates are detected by the green flame produced by volatile methyl (or ethyl) borate on burning (*Methyl Borate test*). (ii) Compounds containing boron, when mixed with $CaF_2$ and conc. $H_2SO_4$ and the mixture heated, give boron trifluoride which burns with a green flame. Quantitatively, boric acid may be estimated by titrating with a standard alkali in presence of some polyhydric alcohols like glycerol or mannitol.

## ALUMINIUM

*Symbol* : Al ; *Atomic No.*=13 ; *Atomic wt.*=26.97
*Electronic configuration* : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$.

OCCURRENCE : Aluminium never occurs native. In the combined state, it is the most abundant metal (ranked as the third most abundant of all the elements). It mainly exists in the form of double silicates as in **Felspar, Kaolin, Mica, Granite and basalt.** The anhydrous oxide occurs as **Corundum** and **Emery** ($Al_2O_3$). The natural gem-stones **Sapphire** (*blue*), **Ruby** (*red*) are also anhydrous oxides tinted by the presence of other metals. The oxide hydrates like **Diaspore** ($Al_2O_3.H_2O$), **Bauxite** ($Al_2O_3.2H_2O$), **Gibbsite** ($Al_2O_3.3H_2O$) occur in large amounts, of which bauxite is used as the chief material for the extraction of the metal. The fluoride occurs as **Cryolite** ($AlF_3.3NaF$) and it is an important adjunct in the metallurgy of aluminium from bauxite. The aluminates exist as **Spinel** ($MgO.Al_2O_3$), **Crysoberyl** ($BeO.Al_2O_3$), and the sulphate, as **Alunite** [$Al_2(SO_4)_3.K_2SO_4.4Al(OH)_3$].

**Indian ores** : India possesses large deposits of bauxite in Bihar, Orissa, Andhra Pradesh (East coast bauxite deposits), Uttar Pradesh, Rajasthan, Tamilnadu, Jammu and Kashmir, Gujrat, Madhya Pradesh *etc*. The metal is extracted in large quantities at Asansol (W. Bengal), Alwaye (Kerala), Hirakud (Orissa), Rihand Dam (Uttar Pradesh) and in many other plants.

EXTRACTION : The industrial production of aluminium is chiefly made by the electrolytic decomposition of pure aluminium oxide (mixed with $CaF_2$), dissolved in molten cryolyte **(Method of Hall and Heroult).**

Aluminium cannot be extracted by the carbon-reduction of pure $Al_2O_3$ at high temperatures, due to the simultaneous formation of some amount of aluminium carbide ($Al_4C_3$) which remains contaminated with the metal produced.

Electrolysis of pure $Al_2O_3$ alone is rendered practically inapplicable due to (i) the high power-consumption to keep $Al_2O_3$ in the molten condition (m.p. of $Al_2O_3$ is $\sim$2050°C) and the considerable volatilisation of the metal at such high temperatures and (ii) the considerably low density of the metal (molten at such temperatures), causing it to float on the surface of the molten electrolyte, and thus making it unsuitable to tap out through the tap-hole near the bottom of the electrolytic cell.

**Purification of bauxite :**

Naturally occuring bauxite is contaminated to a greater or less extent with silica and iron oxide. For the preparation of pure $Al_2O_3$, suitable for the electrolytic extraction of the metal, bauxites are, therefore, to be freed from these two impurities. In the older dry method **(Hall's method)**, finely ground bauxite was heated at about 1100°C with sodium carbonate in a ratory kiln. Sodium aluminate, sodium silicate and sodium ferrite were formed in this process :

$$Al_2O_3+Na_2CO_3=2NaAlO_2+CO_2;$$
$$SiO_2+Na_2CO_3=Na_2SiO_3+CO_2;$$
$$Fe_2O_3+Na_2CO_3=2NaFeO_2+CO_2.$$

The cooled mass was then digested with water at about 80°C, when sodium aluminate passed into solution, sodium ferrite was hydrolysed to ferric oxide and sodium silicate reacted with some sodium aluminate to form insoluble sodium aluminosilicate : $NaFeO_2+2H_2O=Fe(OH)_3+NaOH$. The precipitated ferric hydroxide and sodium aluminosilicate (*red mud*) were filtered and the sodium aluminate in the filtrate was treated with $CO_2$ at 50-60°C, when it decomposed into aluminium hydroxide and sodium carbonate : $2NaAlO_2+CO_2+3H_2O=2Al(OH)_3+Na_2CO_3$. The precipitated $Al(OH)_3$ was ignited at about 1100°C to obtain pure $Al_2O_3$. [The $Na_2CO_3$ formed in solution may be recovered by evaporation and used again.] In a variation of the process, bauxite was heated with $Na_2CO_3$ and CaO, when silica was eliminated as insoluble calcium silicate and $Fe_2O_3$ was transformed into $Fe(OH)_3$, through sodium ferrite as described above. The loss of some aluminium as the insoluble sodium aluminosilicate is minimised by this procedure.

**Serpek Process** was much used earlier for purifying bauxite. But, as the process is obsolete now, a bare outline of the same is mentioned here.

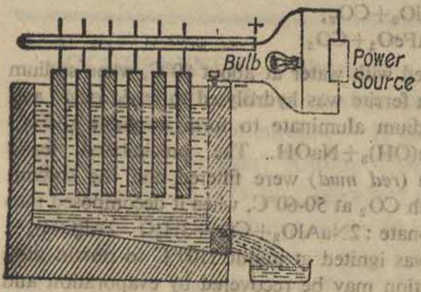
In this process, powdered bauxite was mixed with coke, and the mixture was heated at about 1800°C in a current of nitrogen gas. Aluminium nitride was formed in the process and this was decomposed by boiling with caustic soda solution to $Al(OH)_3$, which was then ignited to pure $Al_2O_3$.

$$Al_2O_3+3C+N_2=2AlN+3CO\ ;\ AlN+3H_2O=Al(OH)_3+NH_3.$$

In the modern wet process **(Bayer Process)**, bauxite is purified by digesting it at 150°C and under pressure with a concentrated solution of NaOH (*sp. gr.* 1.45) for about 5-6 hours. Aluminium oxide goes into solution as sodium aluminate, while the impurities remain as residue. The mixture is filtered and the filtrate is diluted with water and cooled to ordinary temperature ($\simeq$ 30°C). The metastable aluminate solution is decomposed by *seeding* with freshly prepared aluminium hydroxide and agitating the mixture for a few hours. The added $Al(OH)_3$ accelerates the decomposition of sodium aluminate by providing nuclei for crystallisation of the hydroxide formed. The precipitated $Al(OH)_3$ is filtered, washed with water and ignited (1100°C), when pure $Al_2O_3$ is obtained : $Al_2O_3+2NaOH=2NaAlO_2+H_2O$; $2NaAlO_2+4H_2O=2Al(OH)_3+2NaOH$ ; $2Al(OH)_3=Al_2O_3+3H_2O$.

[Caustic soda re-formed during the decomposition of the aluminate may be used again in the process.]

**Electrolysis of the purified bauxite** : A mixture of 20 parts purified bauxite, 60 parts cryolite and 20 parts fluorspar (calcium fluoride)* is electrolysed in a cell which is a carbon-lined iron tank that acts as the cathode. The anodes are stout carbon rods which hang from an adjustable copper frame into the tank. A tap-hole is provided at the bottom of the tank to remove molten aluminium.



Aluminium extraction

In starting up the process, contact is made between the anodes and the bottom of the tank and the electrolyte mixture is added round the contacts. Further additions of the mixture are made when the previous added charge has melted and this is continued till the tank is full. The anodes are then raised and the electrolysis is carried on at about 950°C. Aluminium is liberated at the cathode and it sinks in the molten state to the bottom of the tank and is taken out at intervals. Oxygen is liberated at the anodes, and major part of it combines with the carbon anodes which burn out as CO and $CO_2$. To minimize the oxidation of the expensive anodes, powdered coke is frequently sprinkled over the surface of the molten electrolyle.

$Al_2O_3 \rightleftharpoons 2Al^{+3}+3O^{2-}$ ; $2Al^{+3}+6e=2Al$ (at *cathode*) ;
$3O^{2-}-6e=3[O]$ ; $6[O]=3O_2$ (at *anode*).

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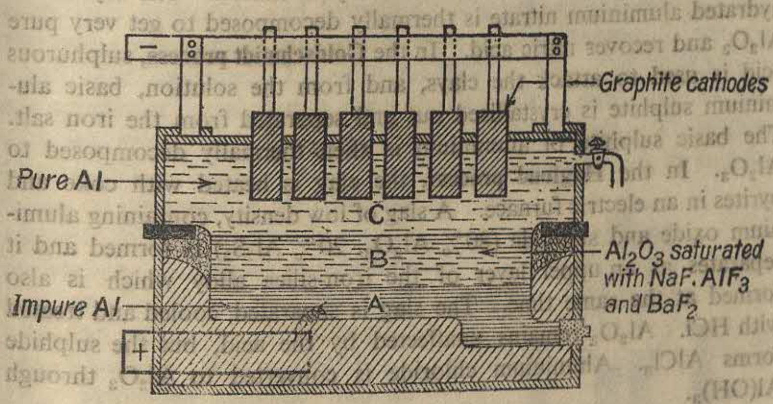
*$CaF_2$ is added to increase the fluidity of the melt or to decrease the melting point of the mixture and also to lower the density of the melt.

The gradual depletion of aluminium of the electrolyte during electrolysis increases its resistance, which is indicated by a glow lamp. Fresh supplies of alumina are then added and the process is thus made continuous. The method produces 99% pure aluminium.

[India possesses large deposits of bauxite, but no cryolite. It is, therefore, prepared synthetically in this country by the interaction of aluminium fluoride, ammonium fluoride and sodium nitrate :
$AlF_3+3NH_4F+3NaNO_3=AlF_3.3NaF+3NH_4NO_3$.]

**Refinining of crude aluminium** : Aluminium extracted in the above process contains small quantities of iron and silicon as impurities. To prepare the high-grade metal, the crude aluminium is refined electrolytically by **Hoope's process.** The refining is carried out in an iron tank, lined with blocks of carbon. It contains three molten layers, *viz.* (i) the layer (A) of the molten crude aluminium at the bottom (directly transferred from the extraction-cell) which acts as the anode, (ii) the middle layer (B) of a molten mixture of cryolite, aluminium oxide and barium fluoride and (iii) the top layer (C) of molten pure aluminium. A number of graphite rods, suspended in the uppermost layer, acts as the cathode. On passing electric current, aluminium ions are formed at the anode and they dissolve in the molten adjacent layer (B), causing an equivalent amount of pure aluminium metal produced in the cathode (C). The impurities are left in the bottom layer and the pure metal (~99.99%) is collected from time to time from the top layer.



Refining of aluminium.

**Extraction of Aluminium from silicate ores or clays** : India has plenty of good quality bauxite and hence aluminium is solely extracted from this ore. Some other countries, who depend mainly on imported bauxite to obtain the metal, had to develop methods to extract aluminium from silicate ores or clays. Such minerals cannot obviously be worked up by alkaline attack, due to the existence of high proportions of silica in them, which is also taken into solution by such method and presents difficulty in the isolation of the pure metal. These are, therefore, worked up by attacking with acids. The acid treatment is so controlled as to avoid the dissolution of iron oxide as far as practicable, since the subsequent separation of large amounts of iron from aluminium presents much difficulty. In the **Buchner or Nuvalone** process, silicate minerals are digested in autoclaves with controlled amount and concentration of $HNO_3$, so that $Al_2O_3$ dissolves as aluminium nitrate, leaving most of $Fe_2O_3$, $SiO_2$ (and $TiO_2$) unaffected. The solution obtained contains aluminium nitrate together with nitrates of alkali and alkaline earth metals, from which the former is separated by fractional crystallisation. The crystals of hydrated aluminium nitrate is thermally decomposed to get very pure $Al_2O_3$ and recover nitric acid. In the **Goldschmidt process,** sulphurous acid is used to attack the clays, and from the solution, basic aluminium sulphite is crystallised out and separated from the iron salt. The basic sulphite of aluminium is then thermally decomposed to $Al_2O_3$. In the **Haglund process,** the clay is heated with coke and pyrites in an electric furnace. A slag of low density, containing aluminium oxide and sulphide (80% $Al_2O_3$, 20% $Al_2S_3$) is formed and it separates as an upper layer of the iron-silica alloy which is also formed at the same time. The slag is separated, cooled and treated with HCl. $Al_2O_3$ remains unaffected by the acid, but the sulphide forms $AlCl_3$. Aluminium chloride is converted to $Al_2O_3$ through $Al(OH)_3$.

In the **Anchor lime sinter process,** powdered silicate minerals or clays are mixed with finely ground limestone, and a slury of them is heated in a kiln at about 1400°C. The mass is sintered, and simultaneous formation of dicalcium silicate takes place. The mass is leached with alkaline sodium aluminate solution (from previous batches) and filtered. The filtrate contains most of the aluminium of the sintered mass as sodium aluminate. It is diluted and seeded with hydrated aluminium oxide, and $CO_2$ is passed at the same time. Pure $Al(OH)_3$ is thus precipitated, which is converted to $Al_2O_3$ by heating. The filtrate of the later operation is used for leaching fresh batch of the sintered mass.

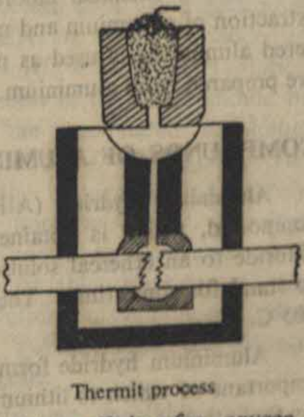
Aluminium oxide, obtained in any one of the above methods, is then subjected to the electrolytic process already described, to obtain the metal.

**Properties :** A silver-white metal of density 2.70, aluminium melts at 660°C and boils at 2270°C. It is a soft and tough metal ; but, it becomes malleable and ductile at 100–150°C and can be transformed into extremely thin foils. The thermal and electrical conductivities of aluminium are quite high (about half of copper).

Pure aluminium is not corroded by dry air ; in moist air, the metal becomes covered with a thin film of oxide, which protects it from further attack. Finely divided aluminium powder catches fire when strongly heated in air and burns with a dazzling white flame, producing mainly $Al_2O_3$ and a small amount of aluminium nitride :

$$4Al+3O_2=2Al_2O_3\ ;\ 2Al+N_2=2AlN.$$

At ordinary temperatures, pure aluminium is not attacked by water ; but, aluminium powder decomposes boiling water, forming aluminium hydroxide and hydrogen : $2Al+6H_2O=2Al(OH)_3+3H_2$. The metal dissolves in HCl (both dilute and concentrated) with the evolution of hydrogen : $2Al+6HCl=2AlCl_3+3H_2$. Dil. $H_2SO_4$ does not attack the metal, but it dissolves on boiling with conc. $H_2SO_4$, with the evolution of sulphur dioxide : $2Al+6H_2SO_4=Al_2(SO_4)_3+6H_2O+3SO_2$. Nitric acid, both dilute and concentrated, is without action on the metal in the cold, but vigorous reaction eventually sets in on heating. Strong alkali solutions dissolve aluminium as aluminates, with the evolution of hydrogen : $2Al+2NaOH+2H_2O = 2NaAlO_2+3H_2$. Hydrogen sulphide has no action on the metal. At elevated temperatures, aluminium reacts with carbon, nitrogen, sulphur and halogens to form the carbide, nitride, sulphide and halides respectively : $4Al+3C=Al_4C_3\ ;\ 2Al+N_2=2AlN\ ;\ 2Al+3S=Al_2S_3\ ;\ 2Al+3X_2=2AlX_3$ (where X=a halogen). Because of its high affinity for oxygen, aluminium is used as a reducing agent to liberate metals from their difficultly reducible oxides, and also for attaining high temperatures, *e.g.* for welding iron. Thus, a mixture of ferric oxide (or oxides of chromium and manganese) and aluminium powder, on ignition with a magnesium ribbon and a primer of barium peroxide and magnesium



Thermit process

powder, reacts violently, with the production of aluminium oxide, while the oxide of the other metal is reduced to the metallic state. Large amount of heat is evolved during the reaction and the metal is obtained in the molten condition. *Goldschmidt's Thermit process* or *the Aluminothermic process* employs a mixture of iron powder and fine granules of aluminium to weld broken iron rails or iron beams by this method. The advantage of such a method is that, the broken object can be repaired without removing it from its place of existence. It is also used in the metallurgy of chromium and manganese : $Fe_2O_3+2Al=Al_2O_3+2Fe$ ; $Cr_2O_3+2Al=Al_2O_3+2Cr$.

**Alloys of aluminium :** Due to its lightness, aluminium is used to prepare many light alloys with high tensile strength for aircraft and automobile industries. Some important alloys of aluminium are ; (i) *magnalium* (90—92% Al, 8—10% Mg), (ii) *duralumin* (93—95% Al, 2.5—5% Cu, 0.5—2% Mg and 0.5—1% Si), (iii) *Scleron* (80—85% Al, 12% Zn, 3% Cu, 0.6% Mn, 0.5% Fe, 0.5% Si and a little amount of Li), (iv) *Aluminium bronze* (10% Al, 90% Cu), (v) *Alnica* (50% steel, 20% Ni, 20% Al and 10% Co).

**Uses :** Aluminium is largely used for the manufacture of industrial apparatus and domestic utensils. Aluminium sheets are used in roofing and in making bodies of air-crafts, antomobiles, speed boats *etc.* Costlier copper has been replaced by aluminium for making electric wires for power transmission. As a reducing agent, it is used in chemical laboratories, and also in metallurgy for the extraction of chromium and manganese by the *Thermit process*. Powdered aluminium is used as paints. A large number of useful alloys are prepared from aluminium.

## COMPOUNDS OF ALUMINIUM.

**Aluminium Hydride,** $(AlH_3)_x$, is a white, amorphous polymeric compound, which is obtained by adding a solution of aluminium chloride to an ethereal solution of $LiAlH_4$ and allowing the mixture to stand for some time. The compound begins to decompose above 105°C.

Aluminium hydride forms complex hydrides (*alanates*), the most important of which is lithium aluminium hydride, which is prepared by the interaction between $AlCl_2$ and LiH in ether solution : $4LiH+AlCl_3=LiAlH_4+3LiCl$. It is a white solid, decomposing into LiH, $H_2$ and Al when heated to 125°C in vacuum. It is soluble in ether, the solution being metastable and decomposing catalytically by powdered metals. It is a valuable reagent in preparative inorganic chemistry and an excellent hydrogenating agent in organic chemistry.

**Aluminium Oxide, Alumina, $Al_2O_3$,** is widely distributed in nature. Colourless crystalline *corundum* and opaque *emery* are anhydrous $Al_2O_3$, as also the coloured gem-stones like amethyst, emerald, ruby, sapphire, topaz *etc.* Hydrated oxide occurs in the minerals *diaspore*, *bauxite* and *gibbsite*. It can be prepared by the combustion of aluminium, or by igniting aluminium hydroxide or some salts of aluminium : $4Al+3O_2=2Al_2O_3$ ; $2Al(OH)_3=Al_2O_3+3H_2O$ ; $2Al_2(SO_4)_3=2Al_2O_3+6SO_2+3O_2$.

Aluminium oxide is a white amorphous powder, insoluble in water, but soluble both in acids and alkalis due to its amphoteric character : $Al_2O_3+6HCl=2AlCl_3+3H_2O$ ; $Al_2O_3+2NaOH=2NaAlO_2+H_2O$. If ignited at high temperatures (>850°C), $Al_2O_3$ becomes insoluble in acids also. Aluminium oxide is highly refractory in nature.

Corundum is used for making highly refractory bricks for furnace-lining. Powdered emery is used in polishing metals. Purified bauxite is used for the extraction of aluminium. *Alundum* (a refractory material), *alums*, *bauxite cement* are also manufactured from bauxite. Since corundum can be artificially prepared by the Thermit process, synthetic gem-stones (both colourless and coloured) can be obtained from it by suitable procedures.

**Aluminium Hydroxide, $Al(OH)_3$,** is formed as a white gelatinous precipitate, when a solution of NaOH, KOH or $NH_4OH$ is added in the cold to a solution of an aluminium salt. [If NaOH or KOH solution is used as the precipitant, addition of excess of the alkali should be avoided to prevent the dissolution of the precipitated aluminium hydroxide]. $Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4$. The amorphous hydrogel, precipitated by the above reaction, slowly changes in contact with solution (and more rapidly on warming) into a crystalline hydroxide, AlO(OH), known as *aluminium metahydroxide.* Heterogeneous materials of variable water-content are obtained by precipitation of acidic solutions of aluminium salts, and these are generally known as *oxide hydrates*, which are distinct from the true hydroxide or the metahydroxide.

Aluminium hydroxide is a white substance, insoluble in water. The freshly prepared material is readily soluble in acids and alkalis, forming aluminium salts and alkali aluminates respectively ; but, on *ageing*, the solubility of the substance in acids and alkalis is much decreased. On heating, it gradually loses water to form various hydrated oxides of aluminium as the intermediate products, and finally gives anhydrous alumina.

Aluminium hydroxide is used in dyeing as a mordant, in removing colloidal impurities from water, in sizing paper and for water-proofing materials.

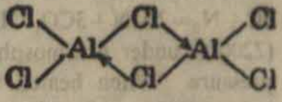
**Aluminium Fluoride, $AlF_3$,** is obtained on passing hydrogen fluoride over red-hot aluminium powder or alumina. The compound is also formed on fusing cryolite with aluminium sulphate and removing sodium sulphate by leaching with water :

$$2Al+6HF=2AlF_3+3H_2 \; ; \; Al_2O_3+6HF=2AlF_3+3H_2O \; ;$$
$$2Na_3AlF_6+Al_2(SO_4)_3=4AlF_3+3Na_2SO_4.$$

Anhydrous aluminium fluoride is a white powder (density=3.1), insoluble in water, acids (except HF) and alkalis. It sublimes at 1291°C without melting. It dissolves in hydrofluoric acid to form complex fluoaluminic acid whose salts (fluoaluminates) are generally formed by the alkali metal or other metal fluorides with aluminium fluoride. These are white crystalline powders, which are insoluble in water. Commercially, the most important fluoaluminate is sodium fluoaluminate or **cryolite** ($Na_3AlF_6$) which occurs native in very large quantities in Greenland. It is obtained as white crystals, relatively easily fusible (1000°C). It is unaffected by acids, but is readily decomposed by boiling alkalis. It is widely used as a flux in the electrolytic reduction of $Al_2O_3$ and in the glass and enamel industries. Cryolite is synthetically prepared by the double decomposition between sodium fluoride and aluminium sulphate, or by adding NaF to a solution of $AlF_3$ in excess of hydrofluoric acid : $12NaF+Al_2(SO_4)_3=3Na_2SO_4+2Na_3AlF_6$ ; $3NaF+AlF_3=Na_3AlF_6$.

**Aluminium Chloride, $AlCl_3$.**—The anhydrous salt is prepared by heating aluminium shavings in a current of dry chlorine or hydrogen chloride gas, or by passing chlorine over a mixture of aluminium oxide and carbon : $2Al+3Cl_2=2AlCl_3$ ; $2Al+6HCl=2AlCl_3+3H_2$ ; $Al_2O_3+3C+3Cl_2=2AlCl_3+3CO$. The product volatilises out and is collected in a cooled receiver. The hydrated salt, $AlCl_3.6H_2O$, can be prepared as colourless, deliquescent crystals, by dissolving aluminium or $Al(OH)_3$ or $Al_2O_3$ in hydrochloric acid and evaporating the solution to crystallisation.

Anhydrous aluminium chloride forms colourless crystalline mass (density=2.44) which sublimes at 183°C, the melting point being 193°C (attainable under pressure only). It is highly deliquescent and fumes strongly in air, due to hydrolysis by atmospheric moisture. It is very soluble in water and the aqueous solution has a strongly acid reaction because of hydrolysis : $AlCl_3+3H_2O \rightleftharpoons Al(OH)_3+3HCl$. The compound is dimeric upto 400°C, and also in benzene solution ; but, it completely dissociates to form the monomer at about 800°C. When dry ammonia gas is passed over anhydrous $AlCl_3$, the hexammine ($AlCl_3.\ 6NH_3$) is formed as a white powder. The anhydrous salt also forms addition compounds with many organic substances, such as acid chlorides, ethers, esters *etc.* The addition products are readily decomposed by water. The hydrated salt decomposes, on heating, to $Al_2O_3$, HCl and water : $2AlCl_3.6H_2O=Al_2O_3+6HCl+3H_2O$.



Dimer of $AlCl_3$

Anhydrous $AlCl_3$ is used as a catalyst in synthetic organic chemistry. It is also used in dye-stuff and essence industries, and for the cracking of petroleum.

**Aluminium Bromide, $AlBr_3.\ 6H_2O$,** is prepared by the method similar to that of $AlCl.6H_2O$. It forms colourless leaflets (density=3.2), melting at 97.5°C and boiling at 265°C. It resembles the chloride in its chemical poperties.

**Aluminium Iodide, $AlI_3$,** is also similar to the chloride or the bromide in properties, and is similarly prepared. Its density is 3.95 and it melts at 191°C. The volatility of the halides is increased and their stability decreases as we pass from chloride through bromide to iodide.

**Aluminium Nitrate, $Al(NO_3)_3$,** is prepared as the hydrated salt, $Al(NO_3)_3.\ 9H_2O$, by dissolving freshly precipitated $Al(OH)_3$ in dilute $HNO_3$, and evaporating the resultant solution to crystallisation. It is also obtained by the reaction between solutions of aluminium sulphate and lead nitrate, when the insoluble lead sulphate is precipitated and aluminium nitrate is formed in solution. The precipitated $PbSO_4$ is filtered off and the clear filtrate is concentrated to crystallise out the hydrated salt : $Al(OH)_3+3HNO_3=Al(NO_3)_3+3H_2O$ ; $3Pb(NO_3)_2+Al_2(SO_4)_3=3PbSO_4\downarrow+2Al(NO_3)_3$.

Aluminium nitrate forms colourless crystals which are extremely deliquescent and highly soluble in water. The aqueous solution of the salt is acidic due to considerable hydrolysis. The compound decomposes into $Al_2O_3$, $NO_2$ and $O_2$ on heating : $4Al(NO_3)_3=2Al_2O_3+12NO_2+3O_2$.

It is used as a mordant in dyeing industry.

**Aluminium Nitride, AlN,** is obtained by heating a mixture of alumina and coke with nitrogen gas in an electric furnace : $Al_2O_3+3C+N_2=2AlN+3CO$. It decomposes below its melting point (2200°C under 4 atmospheres pressure) when heated under ordinary pressure. When heated with caustic soda solution under pressure, it forms $NH_3$ and sodium aluminate.

**Aluminium Carbide, $Al_4C_3$,** is obtained by heating a mixture of aluminium powder and coke at a high temperature. It vaporises above 2200°C. It is decomposed by warm water (or better by dil. acids) to form methane : $Al_4C_3+12H_2O=4Al(OH)_3+3CH_4$.

**Aluminium Carbonate** is not known to exist due to the very weak basicity of $Al_2O_3$.

**Aluminium Sulphide, $Al_2S_3$,** may be prepared by the direct union of aluminium powder and sulphur at a high termperature. It may be obtained as a crystalline solid (density=2.37), melting at 1100°C. It is completely hydrolysed by water, liberating $H_2S$ : $Al_2S_3+6H_2O=2Al(OH)_3+3H_2S$.

**Aluminium Sulphate, $Al_2(SO_4)_3$.**—The hydrated variety of the salt, $Al_2(SO_4)_3 . 18H_2O$, is prepared by dissolving pure $Al_2O_3$ or $Al(OH)_3$ in dilute $H_2SO_4$, and evaporating the solution to crystallisation. In the industrial preparation of the material, powdered bauxite is heated with hot, dilute $H_2SO_4$, or finely ground china-clay (kaolin) is heated with conc. $H_2SO_4$. The mixture is cooled, diluted with water and filtered. From the filtrate, the crystals of $Al_2(SO_4)_3 . 18H_2O$ are obtained by evaporation. Aluminium sulphate, prepared in this way, is often contaminated with ferric sulphate as impurity : $Al_2O_3+3H_2SO_4=Al_2(SO_4)_3+3H_2O$.

Anhydrous aluminium sulphate may be obtained as a white powder (density-2.71), by gently heating the hydrated salt. On stronger heating, however, $Al_2(SO_4)_3$ decomposes into alumina, sulphur dioxide and oxygen : $2Al_2(SO_4)_3=2Al_2O_3+6SO_2+3O_2$. The hydrated aluminium sulphate, $Al_2(SO_4)_3 . 18H_2O$, forms colourless crystals (density 1.62) and has an astringent taste. It is very soluble in water and the aqueous solution is acidic due to hydrolysis : $Al_2(SO_4)_3+6H_2O \rightleftharpoons 2Al(OH)_3+3H_2SO_4$. Aluminium sulphate forms double salts (double sulphates or *alums*) of general composition, $M_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ ($M=K^+$, $NH_4^+$, $Ag^+$ *etc.*), when a mixture of solutions of the two sulphates is allowed to crystallise.

Aluminium sulphate is used as a mordant in dyeing and calico-printing, in sizing paper (in paper industries) and in tanning leather.

It is also used in clarifying muddy water and for the preparation of fire-extinguishing foams.

**Alums** : These are double salts, generally of alkali metal sulphates and aluminium sulphate, and have the empirical formula, $MAl(SO_4)_2$. $12H_2O$, where M is an alkali metal. (The empirical formula, on doubling, gives the molecular formula of alums.) The monovalent alkali metal ion may be replaced by $NH_4^+$ or $Tl^+$, and $Al^{+++}$ may be replaced by other tervalent metal ions such as $Fe^{+++}$ or $Cr^{+++}$ (when these are called ferric alum and chrome alum respectively). So, the general empirical formula of an alum is $M^IM^{III}(SO_4)_2$. $12H_2O$. The alums are formed as regular crystalline solids (octahedral or cubic), which are soluble in water.

Common or ordinary alum (after whose name this group of double salts is so called) is potassium aluminium sulphate, $KAl(SO_4)_2$. $12H_2O$, or $K_2SO_4.Al_2(SO_4)_3.24H_2O$. It may be obtained by crystallising a mixture of equimolar aqueous solutions of potassium sulphate and aluminium sulphate. It is generally manufactured from bauxite. Powdered bauxite is heated with about 62% $H_2SO_4$ in lead-lined steel tanks and a solution is made. The solution is treated with powdered barium sulphide to reduce the ferric salts to the ferrous state and allowed to settle, when $BaSO_4$ precipitates out. The clear supernatant liquid is decanted and mixed with calculated amount of $K_2SO_4$ solution. The mixture is concentrated and cooled, when crystals of common alum separate out. These are filtered, dried and collected.

Common alum forms colourless, octahedral or cubic crystals, soluble in water. Its density is 1.75 and it melts at 92.5°C in its own water of crystallisation. It has a sour astringent taste. The hydrated salt may be completely dehydrated by proper heating. It is insoluble in absolute alcohol.

Common alum is industrially used for the same purposes as is the simple aluminium sulphate. Thus, it finds applications in (i) clarification and purification of water, (ii) as a mordant in dyeing and calico-printing, (iii) in the sizing of paper, (iv) in tanning of leather and (v) as a disinfectant, and for stopping bleeding in minor cuts, as well as an astringent and mild caustic in medicine.

**Aluminium Phosphate**, $AlPO_4$, is obtained as a white gelatinous precipitate by the action of sodium phosphate solution on a neutral [illegible] of an aluminium salt. It is insoluble in water and acetic acid, but soluble in [illegible] acids and alkalis.

## ALUMINOSILICATES.

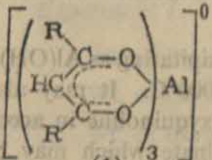
A three-dimensional silicon-oxygen framework, built up in such a way that each oxygen atom is part of two $SiO_4$-tetrahedra, represents the electrically neutral giant-molecule of the composition

$SiO_2$ (silica). If in such a giant molecule, some of the silicon atoms are replaced by aluminium (the oxygens being left unaffected), a negetively charged complex **aluminosilicate** ion results, and this requires cations like sodium, potassium *etc.* for electrical neutrality. If one quarter of the silicons is replaced by aluminium, the complex anion can be represented as $(AlSi_3O_8)^-$, while the replacement of half the silicons by aluminium gives $(Al_2Si_2O_8)^{2-}$. Such unlimited mixed frameworks are present in many natural aluminosilicate minerals, of which the most important are the **felspars, zeolites, ultramarines** *etc.* The three-dimensional Si-O network in these materials involves rings of six tetrahedra, built together to form an extended honeycomb-like structure of high symmetry, with wide channels and cages into which gases and liquids (like water) can enter, and into which cations can diffuse. Such a structure endows these substances with the property of absorbing gases and liquids, enables the hydrated materials to lose water or to re-hydrate without undergoing any change in properties, and this is responsible for their capacity for base-exchange (as in the softening of water by the permutits).

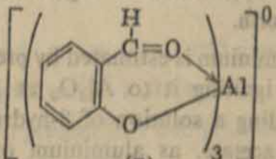
**Ultramarines** : The most interesting among the aluminosilicate minerals is the blue ultramarine which is sodium aluminosilicate, containing sulphur. The deep blue mineral **lazurite** (commonly known as *lapis lazuli*), whose valuable deposits were in Afghanistan, was largely used as semi-precious gem and as valuable pigment in the past. The blue principle of *lapis lazuli* is ultramarine blue. [The word *ultramarine* means 'the blue from beyond the seas', as it was imported to Europe from the East.] The ultramarine of commerce is now-a-days manufactured entirely by artificial synthetic procedures. By suitable variation of methods, ultramarine of any colour, *viz.* white, blue, blue-green, red or violet, may be prepared artificially. Ultramarine is manufactured by heating powdered kaolin to redness in the absence of air with sulphur powder (or sodium sulphate and carbonaceous reducing agent). The resultant yellow-green mass is re-heated in air, when the colour deepens and finally becomes deep blue. Soluble sodium salt is leached out from the cooled mass to obtain the pigment.

The composition of *lapis lazuli* is $Na_{10}Al_6Si_6O_{24}S_6$. But, the composition of synthetic ultramarine is variable, depending upon the method of manufacture. The blue product, obtained in different processes, has been found to have compositions such as $Na_6Al_6Si_6O_{24}S_2$, $Na_7Al_6Si_6O_{24}S_3$, $Na_8Al_6Si_6O_{24}S_4$ *etc.* The alkali metal in the molecule of ultramarine is exchangeable with other bases. Thus, the blue sodium salt reacts with $AgNO_3$ to give yellow silver ultramarine, from which ultramarines containing other metal atoms can be prepared. Ultramarine is fairly stable towards alkalis, but acids break down the molecule, with the liberation of S and $H_2S$. Water, under pressure at 300°C, extracts sodium sulphide from ultramarine, leaving a colourless product. Chlorination of ultramarine at 400°C removes alkali and gives colourless products. The structure of ultramarines, especially the mode of presence of sulphur in the molecules, has been a subject-matter of much research, but the true origin of the intense blue colour still appears to be unexplained. The chemical properties, X-ray structure determination and other physical studies suggest that the colour is associated with the presence of regulated amounts of alkali and of sulphur,—the latter being present partly as sulphide ions and partly as polysulphides, and the structure of ultramarines is similar to that of zeolites with wide channels and cavities.

**Complexes of Aluminium** : Complex compounds containing both octahedrally and tetrahedrally coordinated aluminium are known, the former being more numerous. Of the tetrahedral complexes, $(AlCl_4)^-$ and $(AlBr_4)^-$ are fairly common, although complexes with coordinated neutral ligands like $NH_3$, $PH_3$, amines and phosphines, ethers, thioethers, alcohols, ketones *etc.* are also well-characterised. Octahedral complexes of aluminium with neutral ligands are best illustrated by hexaaquo-aluminium(III), $[Al(H_2O)_6]^{+3}$ and hexadimethyl sulphoxide aluminium(III), $\{Al[OS(CH_3)_2]_6\}^{+3}$. Complex aluminium hexafluorides, $AlF_6^{3-}$ are well-known, of which cryolite, $Na_3[AlF_6]$, is technologically the most important compound. Among



(A)



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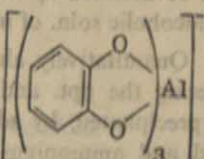
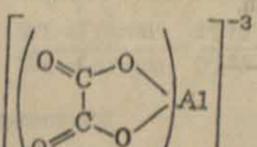
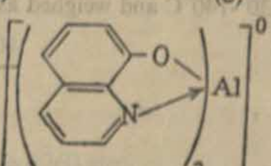


(C)



(D)



(E)

the other octahedral aluminium complexes, the most prominent are those containing chelate rings. Typical of them are complexes with β-diketones (A), salicylaldehyde (B), catechol (C), dicarboxylic acids (such as oxalic acid) (D), 8-hydroxyquinoline (E) *etc.* The neutral complexes are all insoluble in water, but soluble in organic solvents. The anionic complexes have been isolated as salts of appropriate large cations. The complex with 8-hydroxyquinoline is largely used for the estimation of the metal.

**Tests** : (i) An aluminium salt, when mixed with anhydrous $Na_2CO_3$ and heated on a charcoal-block under a reducing flame, produces a white, incandescent mass. This is moistened with a drop of dil. cobalt nitrate soln. and then heated in an oxidising flame. A blue mass (**Thenard's blue**) is obtained. (ii) When a soln. of an aluminium salt is treated with $NH_4OH$ soln., a gelatinous white ppt. of $Al(OH)_3$ is obtained. The ppt. is insoluble in excess of $NH_4OH$ soln. (iii) To a soln. of an aluminium salt, caustic soda soln. is added gradually. A white gelatinous ppt. of $Al(OH)_3$ is first formed, which dissolves in excess of the precipitant, giving a clear solution of sodium aluminate. On boiling this clear soln. with $NH_4Cl$, the gelatinous ppt. of $Al(OH)_3$ re-appears. (iv) Traces of aluminium in solution can be detected by the appearance of a green fluorescence on adding an alcoholic soln. of **morin**.

Quantitatively, aluminium is estimated by precipitating as $Al(OH)_3$, filtering the ppt. and igniting it to $Al_2O_3$ at 1000°C. It may also be precipitated, by adding a solution of 8-hydroxyquinoline in acetic acid and ammonium acetate, as aluminium oxinate which may be dried at 130°-140°C and weighed as such.

# APPENDIX

## CHEMICAL CALCULATIONS

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### THE LAWS OF CHEMICAL COMBINATION

### (A) THE LAW OF CONSTANT PROPORTIONS.

**Illustration.**

*In an experiment, 1·315 gms. of a metal, on being strongly heated in air, produced 1·640 gms. of its oxide. In a second experiment, 1.010 gms. of the same metal was converted into its nitrate by dissolving in nitric acid. This nitrate, on strong heating, was converted into 1.260 gms. of the corresponding oxide. Show that the results of the two experiments agree with the law of constant proportions.*

**Answer :**

*Experiment 1.*

Wt. of the oxide produced=1·640 gms.

Wt. of the metal used=1·315 gms.

∴ Wt. of oxygen present in 1·640 gms. of the oxide

$=(1{\cdot}640-1{\cdot}315)=0{\cdot}325$ gm.

$$\frac{\text{Wt. of metal}}{\text{Wt. of oxygen}}=\frac{1{\cdot}315}{0{\cdot}325}=4{\cdot}04$$

*Experiment 2.*

Wt. of the oxide produced=1·260 gms.

Wt. of the metal used=1·010 gms.

∴ Wt. of oxygen in 1·260 gms. of oxide

$=(1{\cdot}260-1{\cdot}010)=0{\cdot}250$ gm.

$$\therefore\ \frac{\text{Wt. of metal}}{\text{Wt. of oxygen}}=\frac{1{\cdot}010}{0{\cdot}250}=4{\cdot}04$$

It is clearly seen that, in both the samples of the oxides, the ratio of the metal : oxygen is the same. Thus, the results are in agreement with the law of constant proportions.

### EXERCISES

1. On analysis, samples of silver chloride prepared by different methods, gave the following results :

| | wts. of Ag | wts. of AgCl |
|---|---|---|
| (a) | 91·462 gms. | 121·499 gms. |
| (b) | 108·549 gms. | 144·207 gms. |
| (c) | 69·867 gms. | 92·875 gms. |

Show that the above results agree with the law of constant proportions.

2. 2.4 gms. of copper oxide (obtained by strongly heating copper carbonate), on being reduced in a current of hydrogen, yielded 0·54 gm. of water. 0·8 gm. of copper oxide (obtained by heating copper metal in oxygen) gave 0·18 gm. water on reduction in a current of hydrogen. Are these results agree with the law of constant proportions ?

## (B) THE LAW OF MULTIPLE PROPORTIONS.

**Illustration.**

1. *Iron forms two oxides, ferrous oxide and ferric oxide. Ferric oxide contains 30% of oxygen, while ferrous oxide contains 22·2% of oxygen. Show that the results agree with the law of multiple proportions.*

**Answer :**

$$\% \text{ of Fe in ferrous oxide} = (100-22\cdot2) = 77\cdot8$$

∴ in ferrous oxide, 22·2 parts by wt. of oxygen are combined with 77·8 parts by wt. of Fe.

∴ 1 part by wt. of oxygen is combined with $\frac{77\cdot8}{22\cdot2}=3\cdot504$ parts by wt. of Fe.

In ferric oxide, the percentage of oxygen is 30. Hence, percentage of iron $=(100-30)=70$.

∴ In ferric oxide, 30 parts by wt. of $O_2$ are combined with 70 parts by wt. of Fe.

∴ In ferric oxide, 1 part by wt. of $O_2$ is combined with $\frac{70}{30}=2\cdot333$ parts by wt. of Fe.

Thus, in the ferrous and ferric oxides, 1 part by wt. of oxygen has combined with 3·504 and 2·333 parts by wt. of Fe respectively. Hence, the ratio of these two wts. of iron is $3\cdot504 : 2\cdot333 \simeq 3 : 2$, which is a *simple ratio*.

Thus, the results are in agreement with the law of multiple proportions.

### EXERCISES

1. Carbon is found to form two oxides, CO and $CO_2$. In an experiment, 1 gm. of carbon yielded 3·7 gms. of $CO_2$. On passing CO over heated CuO, it was found that 61·9 gms. of $CO_2$ is formed when loss of wt. suffered by the CuO is 22·5 gms. Deduce the percentage composition of carbon monoxide and show that the results agree with the law of multiple proportions.

2. A metal form two oxides. When heated in a current of hydrogen, 1 gm. of each of the oxides yields 0·798 and 0·888 gm. of the metal. Examine whether the results agree with the law of multiple proportions.

## (C) THE LAW OF RECIPROCAL PROPORTIONS.

**Illustration.**

1. (*a*) *Sulphur combines with its own weight of oxygen to form* $SO_2$ *;* (*b*) *94·1% sulphur is present in* $H_2S$ *;* (*c*) $H_2O$ *contains 88·89% of oxygen. Show that these facts illustrate the law of reciprocal proportions.*

**Answer :**

From (*a*), we know that, 1 gm. sulphur combines with 1 gm. $O_2$.

From (*b*), we find that, 1 gm. sulphur combines with

$$\frac{5\cdot9}{94\cdot1}\text{ gm. } H_2 = 0\cdot063 \text{ gm. of } H_2.$$

Thus, we find that 1 gm. of sulphur has separately combined with 1 gm. of $O_2$ and 0·063 gm. of $H_2$.

The ratio of these two weights is $1 : 0\cdot063 = 16 : 1$.

From (*c*), the wt. ratio of $O_2 : H_2$ in $H_2O$ is $88\cdot89 : 11\cdot11 = 8 : 1$.

Now, the number 16 is a simple multiple of 8. Thus, the given data agree with the law of reciprocal proportions.

### EXERCISES

1. $PH_3$ contains 91·1% P and 8·9% $H_2$ ; water contains 88·8% of $O_2$ and 11·2% of $H_2$ ; $P_4O_6$ contains 43·6% of $O_2$ and 56·4% of P. Show that the above facts conform with the law of reciprocal proportions.

2. Copper sulphide contains 33·5% sulphur ; copper oxide contains 79·9% copper and sulphur trioxide contains 40·1% sulphur. Show that these results agree with the law of reciprocal proportions.

## MOLECULAR WEIGHTS.

### Illustrations.

1. *250 ml. of a gas at N.T.P. weigh 0·7317 gm. The density of hydrogen at N.T.P. is 0·08987 gm. per litre. What is the vapour density of the gas ? Calculate its molecular weight.*

**Answer :**

250 ml. of the given gas at N.T.P. weigh 0·7317 gm.

$\therefore$ 4×250 ml. (1 litre) „ „ „ 4×0·7317 gms. $=2{\cdot}9268$ gms.

But, at N.T.P., the density of $H_2$ is 0·08987 gm/litre.

*i.e.* 1 litre of $H_2$ at N.T.P. weighs 0·08987 gm.

$$\therefore \text{ Vapour density of the given gas}=\frac{2{\cdot}9268}{0{\cdot}08987}=32.$$

$\therefore$ Its molecular wt. $=2\times 32=64$.

2. *0·1022 gm. of a volatile compound yields 55·5 ml. of gas at 27°C and 750 mm. pressure. Find out its molecular wt.*

**Answer :**

$$\text{Volume of the above gas at N.T.P.}=\frac{750\times 55{\cdot}5\times 273}{(273+27)\times 760}\text{ ml.}$$

$$=49{\cdot}84\text{ ml.}$$

At N.T.P., 49·84 ml. gas weigh 0·1022 gms.

$$\therefore \text{ „ „ } 22{\cdot}4 \text{ litres „ „ } \frac{0{\cdot}1022\times 22{\cdot}4\times 1000}{49{\cdot}84}$$

$$=45{\cdot}93\text{ gms.}$$

$\therefore$ The molecular wt. of the gas is 45·93.

### EXERCISES

1. If the density of a gas is 3·17 gms. per litre at N.T.P., what is its molecular weight? [Ans. 71]

2. 0·393 gm. of a gas occupies 227 ml. at 27°C and 750 mm. pressure. Calculate its density relative to that of hydrogen, and its molecular weight. [Ans. 21·58, 43·16]

3. Calculate (*a*) the density of $NH_3$ in gms. per litre at N.T.P. and also (*b*) the mass of 125 ml. of the gas at 15°C and 750 mm. pressure. Density of hydrogen at N.T.P. is 0·09 gm. [Ans. 0·765 gm/litre ; 0·085 gm.]

## EQUIVALENT WEIGHTS.

**Illustration.**

1. *0·15 gm. of zinc displaces 0·5 gm. of silver from silver nitrate solution. Again, it is found that 3·25 gms. of pure zinc, on complete oxidation, yield 4·05 gms. of zinc oxide. Find out the equivalent weights of zinc and silver.*

**Answer :**

Wt. of $ZnO = 4{\cdot}05$ gms. Wt. of $Zn = 3{\cdot}25$ gms.

Hence, the wt. of oxygen combined with zinc

$$= 4{\cdot}05 - 3{\cdot}25 = 0{\cdot}8 \text{ gm.}$$

$$\text{So, the eq. wt. of Zn} = \frac{\text{Wt. of Zn}}{\text{Wt. of } O_2} \times 8 = \frac{3{\cdot}25}{0{\cdot}8} \times 8 = 32{\cdot}5.$$

Again, 0.15 gm. Zn displaced 0·5 gm of Ag.

$$\because \text{ Eq. wt. of Ag} = \frac{\text{Wt. of Ag displaced}}{\text{Wt. of Zn dissolved}} \times \text{Eq. wt. of Zn.}$$

$$= \frac{0{\cdot}5}{0{\cdot}15} \times 32{\cdot}5 = 108{\cdot}3$$

2. *0·1827 gm. of the chloride of a metal is converted to 0·1057 gm. of the oxide on heating. Calculate the equivalent weight of the metal. [Eq. wt. of chlorine=35·5 and that of oxygen=8.].*

**Answer :**

Let '$x$' denote the equivalent weight of the metal. Now, $(x+35{\cdot}5)$ gms. of the chloride of the metal form $(x+8)$ gms. of the oxide.

$$\therefore \quad \frac{(x+8)}{(x+35{\cdot}5)} = \frac{0{\cdot}1057}{0{\cdot}1827},$$

Solving for $x$, we get $x = 29.74$.

$\therefore$ The eq. wt. of the metal is 29.74.

3. *1·0813 gms. of iron gave 3·1439 gms. of ferric chloride. Calculate the equivalent weight of iron in the compound. If the atomic weight of iron is 55.84, find out the valency of iron in ferric chloride.*

**Answer :**

Wt. of chlorine combined with 1·0813 gms. of iron

$$= 3{\cdot}1439 - 1{\cdot}0813 = 2{\cdot}0626 \text{ gms.}$$

2·0626 gms. $Cl_2$ combine with 1·0813 gms. of iron in ferric chloride

$$\therefore \quad 35{\cdot}5 \quad .. \quad Cl_2 \quad .. \quad .. \quad \frac{1{\cdot}0813 \times 35{\cdot}5}{2{\cdot}0626} \quad .. \quad ..$$

$$= 18{\cdot}61 \text{ gms. of iron.}$$

## ACIDIMETRY—ALKALIMETRY.

**Illustrations.**

1. *The equivalent wt. of a substance in 49. How many gms. of this substance must be taken to make 250 ml. of exactly* $\frac{N}{10}$ *solution ? If 1·306 gms of the substance are present in 250 ml. of this solution, find out how much water is to be added to 200 ml. of this solution to make it exactly decinormal.*

**Answer :**

The eq. wt. of the substance is 49.

$\therefore$ 250 ml. of its $\frac{N}{10}$ soln. will contain $\frac{4.9}{4}=1{\cdot}225$ gms. of the substance.

Thus, to make 250 ml. of a $\frac{N}{10}$ solution, 1·225 gms. of the substance will be required.

Again,

250 ml. of the solution contain 1·306 gms. of the substance

$\therefore$ 200 .. .. $\frac{1.306\times 200}{250}$ gms.

$=1{\cdot}0448$ gms. of the substance.

Now, 4·9 gms. of the substance is present in 1000 ml. of its $\frac{N}{10}$ soln.

$\therefore$ 1·0448 gms. .. .. .. $\frac{1000\times 1{\cdot}0448}{4{\cdot}9}$

$=213{\cdot}2$ ml. of its $\frac{N}{10}$ soln.

Here, we see that 200 ml. of the soln. contain the same amount of the substance as should be present in 213·2 ml. of its $\frac{N}{10}$ solution. So, by adding $(213{\cdot}2-200)=13{\cdot}2$ ml. of water, the solution may be made exactly decinormal.

2. *10 gms. of 95% NaOH are dissolved in 200 ml. water. It is then treated with 50 ml. of 1.5 (N) HCl and then the resultant solution is diluted to 500 ml. Find out whether the solution will be acidic or alkaline, and express its strength in terms of normality.*

**Answer :**

10 gms. of 95% NaOH=9·5 gms. pure NaOH.

So, 9·5 gms. NaOH were dissolved in 200 ml. water.

$\therefore$ 1000 ml. soln. contain $\frac{9\cdot5\times1000}{200}=47\cdot5$ gms. NaOH.

So, the strength of the NaOH soln.$=\frac{47\cdot5}{40}=1\cdot1875$ (N).

Now, 200 ml. of 1·1875 (N) NaOH soln.$=(200\times1\cdot1875)$ ml.
of (N) NaOH soln.=237·5 ml. (N) NaOH soln.

Again, 50 ml. of 1·5 (N) HCl$\equiv(50\times1\cdot5)$ ml. (N) HCl=75 ml.
(N)HCl,.

So, in the mixture, $(237\cdot5-75)=162\cdot5$ ml. (N) NaOH soln. will remain unreacted. Let the strength of the resultant solution be $x$, then,

$500\times x=162\cdot5\times1$(N) ;

or $x=\frac{162\cdot5}{500}$ (N)=0·325 (N).

Thus, the resultant mixture will be alkaline and its strength will be 0·325 (N) with respect to NaOH.

3. *In determining the percentage of ammonia in ammonium sulphate, the following results are obtained: 1·216 gms. of the ammonium sulphate was boiled with excess of NaOH and the ammonia evolved was passed through 100 ml. of (N) $H_2SO_4$. The remaining acid required 81·6 ml. of (N) NaOH for complete neutralisation. Calculate the percentage of ammonia in the given ammonium sulphate sample.*

**Answer :**

81·6 ml. (N) NaOH soln.$\equiv$81·6 ml. (N) $H_2SO_4$ soln.

So, out of 100 ml. (N) $H_2SO_4$ soln. used to absorb ammonia, 81·6 ml. remain unreacted.

$\therefore$ Only $(100-81.6)=18\cdot4$ ml. of (N) $H_2SO_4$ soln. reacted with the evolved ammonia.

Now, 18·4 ml. (N) $H_2SO_4$ contain $\frac{18\cdot4}{1000}=0\cdot0184$ gm-equivalent of $H_2SO_4$

But, 0·0184 gm-equivalent of $H_2SO_4$ neutralises 0·0184 gm-equivalent or $(0\cdot0184\times17)$ gms.=0·3128 gm. of $NH_3$.

So, 1·216 gms. of $(NH_4)_2SO_4$ contain 0·3128 gm. $NH_3$

$\therefore$ 100 gms. ,, ,, ,, $\frac{0.3128\times100}{1.216}=25{\cdot}72$ gms. of $NH_3$.

Thus, the percentage of $NH_3$ in ammonium sulphate is 25·72.

### EXERCISES

1. 10·0 gms. of washing soda $(Na_2CO_3.10H_2O)$ are required to neutralise 50 ml. of a sample of HCl solution. How many ml. of this acid must be diluted to 1 litre so that we may get a $\left[\frac{N}{2}\right]$ solution of HCl? [Ans. 358 ml.]

2. 250 ml. of a solution of an acid contain 1·225 gms. of the acid. 25 ml. of this solution is completely neutralised by 20 ml. of $\left[\frac{N}{10}\right]$ NaOH solution. Find out the molecular weight of the acid, if its basicity is 2. [Ans. 122·5]

3. A specimen of limestone contains 60% $CaCO_3$. Calculate the amount of the limestone required to generate carbon dioxide just sufficient to convert 1 litre of $\left[\frac{N}{2}\right]$ NaOH solution into $Na_2CO_3$. [Ans. 41·65 gms.]

4. A mixture contains $Na_2CO_3$, $NaHCO_3$ and NaCl. 2 gms. of this mixture, on gentle heating, liberate 56 ml. of $CO_2$ at N.T.P. Another 2 gms. of the same mixture require 325 ml. of $\left[\frac{N}{10}\right]$ HCl for complete neutralisation. Calculate the percentage of each component in the mixture.
[Ans. $NaHCO_3=21\%$; $Na_2CO_3=72{\cdot}85\%$ and $NaCl=6{\cdot}15\%$]

## EUDIOMETRY.

### Illustrations.

1. *22 ml. oxygen is required for the complete combustion of a mixture of acetylene and marsh gas, and 14 ml. of $CO_2$ is produced as a result of this combustion. Find the volume of marsh gas and acetylene in the given gas-mixture.*

**Answer :**

The chemical formula of marsh gas is $CH_4$ (methane).
Let the vol. of the gas-mixture by $y$ ml. and that of $CH_4$ be $x$ ml.
So, the volume of $C_2H_2=(y-x)$ ml.
The reactions of the combustion are :

$$\begin{array}{llcllcll} (a) & CH_4 & + & 2O_2 & = & CO_2 & + & 2H_2O \\ & \text{1 vol.} & & \text{2 vols.} & & \text{1 vol.} & & \\ \text{and, } (b) & 2C_2H_2 & + & 5O_2 & = & 4\,CO_2 & + & 2H_2O \\ & \text{2 vols.} & & \text{5 vols.} & & \text{4 vols.} & & \end{array}$$

From eqn. (*a*), we get, $x$ ml. $CH_4$ reacts with $2x$ ml. of $O_2$ to form $x$ ml. of $CO_2$.

From eqn. (*b*), we get, $(y-x)$ ml. of $C_2H_2$ react with $\frac{5}{2}(y-x)$ ml. of $O_2$ to form $2(y-x)$ ml. of $CO_2$.

So, the total volume of $O_2$ consumed$=\{2x+\frac{5}{2}(y-x)\}$ ml. and the total volume of $CO_2$ formed$=\{x+2(y-x)\}$ ml.

$\therefore\ 2x+\frac{5}{2}(y-x)=22$ ; or, $5y-x=44$ .. (i)

and $x+2(y-x)=14$ ; or, $2y-x=14$ .. (ii)

From (i) and (ii), we get, $y=10$ and $x=6$.

So, the vol. of the original mixture is 10 ml., of which 6 ml. is $CH_4$ and $(10-6)=4$ ml. is $C_2H_2$.

2. *The composition of a gas-mixture is 50% $H_2$, 40% $CH_4$ and 10% $O_2$. What is the volume of additional oxygen at N.T.P. that will be required for the complete combustion of 200 ml. of the above gas-mixture measured at 27°C and 750 mm. pressure ?*

**Answer :**

Let the vol. of the gas-mixture at N.T.P. be V ml.

$$\therefore\ \frac{200\times750}{300}=\frac{V\times760}{273}\ ;\ \text{or, } V=\frac{200\times750\times273}{300\times760}=179{\cdot}7\text{ ml.}$$

So, at N.T.P., (i) the vol. of $H_2$ in the mixture is

$$179{\cdot}7\times\frac{50}{100}=89{\cdot}85\text{ ml.}$$

(ii) vol. of $CH_4$ in the mixture is

$$179{\cdot}7\times\frac{40}{100}=71{\cdot}88\text{ ml.}$$

and (iii) vol. of $O_2$ in the mixture is

$$179.7\times\frac{10}{100}=17.97\text{ ml.}$$

$$\begin{array}{lllllll} \text{Now,} & 2H_2 & + & O_2 & = & 2H_2O\ ; & \\ & \text{2 vols.} & & \text{1 vol.} & & & \\ & CH_4 & + & 2O_2 & = & CO_2 & +\ 2H_2O \\ & \text{1 vol.} & & \text{2 vols.} & & \text{1 vol.} & \end{array}$$

$\therefore$ 89·85 ml. $H_2$ require $\frac{89{\cdot}85}{2}=44{\cdot}92$ ml. of $O_2$

and 71·88 ml. $CH_4$ require $(71{\cdot}88\times2)=143{\cdot}76$ ml. of $O_2$.

So, total $O_2$ reqd.$=(44{\cdot}92+143{\cdot}76)=188{\cdot}68$ ml.

But, the mixture contained only 17.97 ml. of $O_2$ at N.T.P. ∴ (188.68 − 17.97) = 170.71 ml. of $O_2$ at N.T.P. will be required *in addition to* the oxygen present in the mixture.

3. *A sample of paraffin contains 20% $H_2$ and 80% carbon. If air contains 21% of oxygen (by volume), find out the volume of air, at 27°C and 750 mm. pressure, which will be required for the complete combustion of 60 gms. of the above paraffin.*

**Answer :**

According to the condition of the problem, 60 gms. of the paraffin contain $\frac{60\times 20}{100}=12$ gms. hydrogen and $\frac{60\times 80}{100}=48$ gms. of carbon.

From the eqn., $2H_2+O_2=2H_2O$, we know that, for the complete combustion of 4 gms. of $H_2$, one gm-molecule (32 gms.) or 22·4 litres (at N.T.P.) of oxygen are reqd.

So, 12 gms. of $H_2$ will require $\frac{22{\cdot}4\times 12}{4}=67{\cdot}2$ litres $O_2$ (at N.T.P.).

Again, from the eqn., $C+O_2=CO_2$, we know that, 12 gms. of carbon require, for complete combustion, 1 gm-mole or 22·4 litres of $O_2$ at N.T.P. So, 48 gms. of carbon will require $\frac{22{\cdot}4\times 48}{12}=89{\cdot}6$ litres $O_2$ at N.T.P.

Thus, for the complete combustion of 60 gms. of the given hydrocarbon, 67·2 + 89·6 = 156·8 litres of $O_2$ at N.T.P. will be required.

Now, air contains 21% by volume of $O_2$.

∴ 156·8 litres of $O_2$ at N.T.P. are contained in $\frac{156{\cdot}8\times 100}{21}=746{\cdot}66$ litres of air.

Let this 746·66 litres of air at N.T.P. occupy, at 27°C and 750 mm. pressure, a volume of V litres. So, we write,

$$\frac{746{\cdot}66\times 760}{273}=\frac{V\times 750}{300}$$

$$\text{or,}\quad V=\frac{746{\cdot}66\times 760\times 300}{273\times 750}=831{\cdot}4 \text{ litres.}$$

## EXERCISES

1. 100 ml. of a mixture of CO, $CH_4$ and $H_2$ are mixed with 300 ml. of $O_2$ and exploded. After cooling, the resultant gas occupied 285 ml., and after absorption

by caustic potash solution, 25 ml. oxygen remained. Find the composition of the mixture. [Ans. CO=50 ml.; $CH_4$=30 ml. and $H_2$=20 ml.]

2. 10 ml. of mixture of carbon dioxide, methane and nitrogen were mixed with excess oxygen and exploded, when a contraction of 6.5 ml. in volume takes place. On treatment with KOH solution, the resultant mixture suffers a further contraction of 7 ml. Find out the composition of the original gas-mixture.

[Ans. CO=5 ml.; $CH_4$=2 ml. and $N_2$=3 ml.]

3. A sample of coal gas contains 40% $H_2$, 35% $CH_4$, 15% CO and 10% $C_2H_2$. 100 volumes of this gas were fired with 600 volumes of air, which contained 21% $O_2$. Calculate the composition of the resulting gas-mixture on cooling.

[Ans. $CO_2$=70, $O_2$=3.5 and $N_2$=47.4 vols.]

## ATOMIC STRUCTURE AND ELECTRONIC CONFIGURATION OF ELEMENTS.

### Illustrations.

1. *Calculate the energy-content of one quantum of light with wavelength 600 mμ. Given 1 mμ (millimicron)=10Å.*

**Answer :**

From the eqn. E=hν, we know that the amount of energy in a light quantum is hν, where h is Planck's constant with a value of $6{\cdot}624\times10^{-27}$ erg-sec. and ν is the frequency of the light. The frequency of light (ν) of wavelength λ, is c/λ, where c is the velocity of light and is equal to $3\times10^{10}$ cms. per second. Thus, in this problem,

$$\nu=\frac{3\times10^{10}}{6000\times10^{-8}} \qquad (1\text{Å}=10^{-8}\text{ cms. and } 600\ m\mu = 6000\text{ Å}=6000\times10^{-8}\text{ cms.})$$

$$=5\times10^{14}\text{ cycles/sec.}$$

Putting this value of ν in the eqn. E=*h*ν,

We get, $E=6{\cdot}624\times10^{-27}\times5\times10^{14}$

$=3{\cdot}1120\times10^{-12}$ erg.

2. *Calculate the wavelength associated with an electron accelerated through a potential difference of 10 kilovolts. Given, mass of an electron=$9{\cdot}1085\times10^{-28}$ gm. and 1 electron-volt=$1{\cdot}6018\times10^{-12}$ ergs.*

**Answer :**

The energy acquired by the electron (E) falling through a potential difference of 10 kilovolts is $1{\cdot}6018\times10^{-12}\times10^4$.

Or, $E=1{\cdot}6018\times10^{-8}$ ergs.

The velocity of the electron can now be calculated from the eqn.,

$$E=\tfrac{1}{2}mv^2.$$

$$\text{So,}\quad 1{\cdot}6018\times10^{-8}=\tfrac{1}{2}\times9{\cdot}1085\times10^{-28}\times v^2$$

$$\text{or,}\quad v^2=\frac{2\times1{\cdot}6018\times10^{-8}}{9{\cdot}1085\times10^{-28}}$$

$$\text{or,}\quad v=\sqrt{\frac{3{\cdot}2036\times10^{20}}{9{\cdot}1085}}=0{\cdot}5931\times10^{10}\ \text{cms/sec.}$$

The de Broglie relationship is, $\lambda=\dfrac{h}{mv}$,

where $\lambda$=wavelength of the electron considered as wave, $mv$=momentum of the moving electron and $h$ is the Planck's constant.

$$\text{Thus, here,}\quad \lambda=\frac{6{\cdot}624\times10^{-27}}{9{\cdot}1085\times10^{-28}\times0{\cdot}5931\times10^{10}}$$

$$=1{\cdot}226\times10^{-9}\ \text{cm.}$$

3. *A stream of electrons, travelling with a velocity of 3×10⁹ cms./sec., is deflected while passing through an electric field of 0·06 e.s.u./cm., perpendicular to their path of propagation. If the radius of the deflected path is 300 cms., calculate the value of e/m for the electron.*

**Answer.**

Velocity ($v$) of the electron$=3\times10^9$ cms./sec.

Strength of the deflecting electric field ($X$)$=0{\cdot}06$ e.s.u./cm.

Radius of the deflected path (r)$=300$ cms.

According to the conditions of the problem,

$$\text{here,}\quad \frac{mv^2}{\text{r}}=Xe$$

$$\text{or,}\quad e/m=\frac{v^2}{\text{r}X}=\frac{(3\times10^9)^2}{300\times0{\cdot}06}$$

$$=5\times10^{17}\ \text{e.s.u./gm.}$$

4. *Calculate the velocity with which an electron must revolve round the nucleus of a hydrogen atom so that it may not be pulled into the nucleus by the attraction of the positively charged proton. Given :*

*mass of the electron* ($m$)$=9{\cdot}10\times10^{-28}$ *gm.*

*charge of the electron* ($e$)$=4{\cdot}8\times10^{-10}$ *e.s.u.*

*radius of the electron-orbit* ($r$)$=0{\cdot}5\times10^{-8}$ *cm.*

**Answer :**

Since the charge on the hydrogen nucleus is equal in magnitude but opposite in sign to the charge of the electron, it will tend to pull in the electron towards itself. The condition under which the electron may not be pulled in by the nucleus is such that, the coulombic forces of attraction of the nucleus on the electron is just balanced by the centrifugal force generated on the electron due to its revolution round the nucleus. Thus,

$$\frac{e^2}{r^2}=\frac{mv^2}{r}$$

$$\text{or,}\quad v^2=\frac{e^2}{mr}=\frac{(4\cdot8\times10^{-10})^2}{9\cdot10\times10^{-28}\times0\cdot5\times10^{-8}}$$

$$\text{or,}\quad v=\sqrt{\frac{(4\cdot8\times10^{-10})^2}{9\cdot10\times10^{-28}\times0\cdot5\times10^{-8}}}=2\cdot25\times10^{8}\text{ cms./sec.}$$

5. *Calculate the radius of the first Bohr-orbit of the hydrogen atom. Given :* $h=6\cdot62\times10^{-27}$ *erg.-sec.,* $m=9\cdot11\times10^{-28}$ *gm. and* $e=4\cdot804\times10^{-10}$ *e.s.u.*

**Answer :**

The expression for a Bohr-orbit specified by a principal quantum number '$n$' is,

$$r=\frac{n^2h^2}{4\pi^2mZe^2}.$$

For the first Bohr-orbit, $n=1$, and for hydrogen, $Z=1$.

$$\therefore\quad r_1=\frac{(1\times6\cdot62\times10^{-27})^2}{4\times(3\cdot14)^2\times9\cdot11\times10^{-28}\times(4\cdot804\times10^{-10})^2}$$

$$=0\cdot528\times10^{-8}\text{ cm.}$$

6. *Calculate (a) the radius, (b) the velocity and (c) the energy of an electron in the third Bohr-orbit of the hydrogen atom, using the values of e, m and h given in the previous problems.*

**Answer :**

(*a*) The radius of a Bohr-orbit, sepcified by the principal quantum number $n$, is given by the expression

$$r_n=\frac{n^2h^2}{4\pi^2mZe^2}=\frac{n^2h^2}{4\pi^2me^2}\qquad(\because\ Z=1)$$

Here, $n=3$. $\therefore\quad r_3=\frac{3^2h^2}{4\pi^2me^2}=9\times\frac{h^2}{4\pi^2me^2}.$

From the worked out example number (5), we know that $\dfrac{h^2}{4\pi^2 me^2}$ is a constant and $=0{\cdot}528$ Å.

$\therefore\ r_3=(9\times 0{\cdot}528)$ Å$=4{\cdot}752$ A.

(*b*) For the electron to rotate round the nucleus in a Bohr-orbit, the relation $\dfrac{e^2}{r^2}=\dfrac{mv^2}{r}$ must be satisfied ; *i.e.* we have, $v^2=\dfrac{e^2}{mr}$, where $r$=radius of the orbit.

Here, $r=4{\cdot}752$ Å$=4{\cdot}752\times 10^{-8}$ cms.

$$\therefore\ v^2=\frac{(4{\cdot}8\times 10^{-10})^2}{9{\cdot}10\times 10^{-28}\times 4{\cdot}725\times 10^{-8}}=0{\cdot}5358\times 10^{16}$$

or, $v=0{\cdot}7299\times 10^{8}$ cms./sec.

(*c*) The energy of an electron in a Bohr-orbit, specified by the principal quantum number '*n*', is given by the expression,

$$E_n=-\frac{2\pi^2 e^4 m.}{n^2 h^2}$$

Here $n=3$ ; $\quad\therefore\ E_3=\dfrac{2\pi^2 em^4}{3^2 h^2}=0{\cdot}242\times 10^{-11}$ ergs.

## EXERCISES

1. Calculate the wavelength of an electron whose kinetic energy is 100 ev. [Ans. $1{\cdot}2266\times 10^{-8}$ cm.]

2. An X-ray tube is operated at a voltage of 40,000 V. What is the shortest wavelength of X-rays present in the beam from this tube? [Ans. $1{\cdot}12\times 10^{-9}$ cm.]

3. Calculate the radius of the first Bohr-orbit. Given :

$e\ =\ 4{\cdot}8\times 10^{-10}$ e.s.u.
$m\ =\ 9{\cdot}1\times 10^{-28}$ gm.
$h\ =\ 6{\cdot}62\times 10^{-27}$ erg-sec. [Ans. 0·529 Å]

4. Compute the energy of an electron present in an orbit of the hydrogen atom specified by the principal quantum number 1. Given :

$e\ =\ 4{\cdot}8\times 10^{-10}$ e.s.u.
$m\ =\ 9{\cdot}1\times 10^{-28}$ gm.
$h\ =\ 6{\cdot}62\times 10^{-27}$ erg-sec. [Ans. $2{\cdot}18\times 10^{-11}$ ergs.]

5. Calculate the velocity of the electron in the 2nd Bohr-orbit, using the values of *e* and *h* in the above example. [Ans. $v=1{\cdot}094\times 10^{8}$ cms/sec.]

6. Calculate the frequency ($\nu$) and the wavelength ($\lambda$) of the radiation emitted, when an electron of a hydrogen atom jumps to the ground state from the 3rd Bohr-orbit. Use the values of *e*, *m* and *h* given in the example (3) and $C=3\times 10^{10}$ cms./sec. [Ans. $\nu=0{\cdot}29\times 10^{16}$ ; $\lambda=103$ Å]

## CHEMICAL BONDING.

**Illustrations.**

1. *Given the following data, calculate the crystal-lattice energy (U) of LiF :*

*Ionization energy (I) of Li = 124 Kcals/mole ;*
*Sublimation energy (S) of Li = 38 Kcals/mole ;*
*Electron affinity (E) of F = 81 Kcals/mole ;*
*Dissociation energy (D) of $F_2$ = 135 Kcals/mole ;*
*Heat of formation (Q) of LiF = 146 Kcals/mole.*

**Answer.**

From Born-Haber cycle, we know that,

$$\begin{aligned} U &= Q+S+I+\tfrac{1}{2}D-E \\ &= 146+38+124+67{\cdot}5-81 \text{ Kcals/mole} \\ &= 294{\cdot}5 \text{ Kcals/mole.} \end{aligned}$$

2. *Calculate the electron affinity of chlorine from the following data :*

*Heat of formation (Q) of KCl (s) from K (s) and $Cl_2(g)$=104·9 Kcals/mole ;*
*Heat of sublimation (S) of K=21·7 Kcals/mole ;*
*Heat of dissociation (D) of $Cl_2$=57·8 Kcals/mole ;*
*Ionization energy (I) of K=99·6 Kcals/mole ;*
*Crystal-lattice energy (U) of KCl=164·4 Kcals/mole.*

**Answer.**

We know that, $U=Q+S+I+\tfrac{1}{2}D-E$

or, $$\begin{aligned} E &= Q+S+I+\tfrac{1}{2}D-U \\ &= 104{\cdot}9+21{\cdot}7+99{\cdot}6+28{\cdot}9-164{\cdot}4 \\ &= 90{\cdot}7 \text{ Kcals/mole.} \end{aligned}$$

### EXERCISES

1. A metal M form a crystalline chloride MCl. The sublimation energy of M is 30 Kcals/mole and the formation energy of MCl from the elements is 130 Kcals/mole ; Ionization energy of M is 160 Kcals/mole. Calculate its lattice energy, if the dissociation energy of $Cl_2$ is 54·6 Kcals/mole and its electron affinity is 83·4 Kcals/mole. [Ans. 262·9 Kcals/mole.]

2. Calculate the electron affinity of iodine from the following data :

(*a*) $I_2\,(s) \xrightarrow{\qquad} I_2\,(g) \quad = \quad 15{\cdot}0$ Kcals/mole.
(*b*) $I_2{}^\circ\,(g) \xrightarrow{\qquad} 2\,I^\circ\,(g) \quad = \quad 70{\cdot}8$ Kcals/mole.
(*c*) $I^-\,(g) \xrightarrow{\qquad} I^-\,(aq) \quad = \quad 85{\cdot}8$ Kcals/mole.
(*d*) $\frac{1}{2}\,I_2{}^\circ\,(s)+e \xrightarrow{\qquad} I^-\,(aq) \quad = \quad 114{\cdot}3$ Kcals/mole.

[Ans. 87 Kcals/mole.]

3. Find out the heat of formation of NaCl from the following data :
Lattice energy of NaCl=184 Kcals/mole.
Sublimation energy of sodium=26 Kcals/mole.
Dissociation energy of $Cl_2$=58 Kcals/mole.
Electron affinity of Cl=87 Kcals/mole.
Ionization energy of Na=124 Kcals/mole. [Ans. 92 Kcals/mole.]

## RADIOACTIVITY.

### Illustrations.

1. *A 0.100 mg. sample of Ionium ($Th^{230}$) was found to decay at a rate of $4.32\times10^6$ disintegrations per minute (dpm). What is the half-life of this nucleide ? Calculate its average life.*

**Answer.**

Wt. of Ionium=0·100 mg.=0·0001 gm.

$$\therefore \quad \text{Number of atoms of Ionium}=\frac{0{\cdot}0001\times6{\cdot}03\times10^{23}}{230}=N$$

$$\text{We know that,} \quad \frac{dN}{dt}=\lambda N$$

$$\text{Here,} \quad \frac{dN}{dt}=4{\cdot}32\times10^6\ dpm.$$

$$\therefore \quad 4{\cdot}32\times10^6=\frac{\lambda\times0{\cdot}0001\times6{\cdot}03\times10^{23}}{230}$$

$$\text{or,} \quad \lambda=\frac{4{\cdot}32\times230\times10^6}{6{\cdot}03\times10^{19}}$$

$$=164{\cdot}776\times10^{-13}\ min^{-1}.$$

$$\text{Again, we know that, half-life } T_{\frac{1}{2}}=\frac{0{\cdot}693}{\lambda}$$

$$\text{or, } T_{\frac{1}{2}}=\frac{0{\cdot}693}{164{\cdot}776\times10^{-13}}=4{\cdot}206\times10^{10}\text{ mins.}$$

$$=\frac{4{\cdot}206}{60\times24\times365}\times10^{10}\text{ years.}$$

$$=8\times10^4\text{ years.}$$

$$\text{Average life, } T_{av}=\frac{1}{\lambda}=\frac{1}{164{\cdot}776\times10^{-13}\times60\times24\times365}\text{ yrs.}$$

$$=1{\cdot}16\times10^5\text{ yrs.}$$

2. *The half-life of radon is 3.82 days. What fraction of a freshly separated sample of radon will remain after 1, 4 and 10 days ?*

**Answer.**

The fraction of a radio-element remaining after $n$ half-lives$=(\frac{1}{2})^n$. Here, according to the problem,

$$1 \text{ day}=\frac{1}{3.82}=0{\cdot}264 \text{ half-life.}$$

$$4 \text{ days}=\frac{4}{3.82}=1{\cdot}047 \text{ half-lives.}$$

$$10 \text{ days}=\frac{10}{3.82}=2{\cdot}617 \text{ half-lives.}$$

$\therefore$ Radon remaining after 1 day $=(\frac{1}{2})^{0\cdot264}=0{\cdot}8323$ of the original amount ;

" " " 4 days$=(\frac{1}{2})^{1\cdot047}=0{\cdot}4840$ of the original amount ;

" " " 10 days$=(\frac{1}{2})^{2\cdot617}=0{\cdot}1631$ of the original amount.

3. *An uranium mineral is found to contain one atom of radium for every $2{\cdot}8\times10^6$ atoms of uranium. If the half-life of uranium is $4{\cdot}5\times10^9$ years, find out the value of the half-life of radium.*

**Answer.**

When radioactive equilibrium between a parent and its daughter element is reached, we know that,

$$\lambda_1N_1=\lambda_2N_2$$

$$\text{or,}\quad \frac{N_1}{N_2}=\frac{\lambda_2}{\lambda_1} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (1)$$

$$\text{Also, we know that,}\quad \frac{\lambda_2}{\lambda_1}=\frac{(T_{\frac{1}{2}})_1}{(T_{\frac{1}{2}})_2} \quad \cdots \quad \cdots \quad \cdots \quad (2)$$

$$\text{From (1) and (2), we get,}\quad \frac{N_1}{N_2}=\frac{(T_{\frac{1}{2}})_1}{(T_{\frac{1}{2}})_2} \quad \cdots \quad \cdots \quad \cdots \quad (3)$$

Let the number of atoms of uranium present be denoted by $N_2$ and let $\lambda_2$ denote its disintegration constant. Also, let $N_1$ represent the number of atoms of radium and $\lambda_1$ its disintegration constant. Let also $(T_{\frac{1}{2}})_1$ and $(T_{\frac{1}{2}})_2$ represent half-life of radium and uranium respectively.

∴ According to the data given, from eqn. (3) we get,

$$\frac{1}{2{\cdot}8\times10^6}=\frac{(T_{\frac{1}{2}})_1}{4{\cdot}5\times10^9}$$

$$\therefore\ (T_{\frac{1}{2}})_1=\frac{4{\cdot}5\times10^9}{2{\cdot}8\times10^6}=1607 \text{ years.}$$

4. *The $_6C^{14}$ : $_6C^{12}$ ratio in a certain piece of fossilised wood, obtained from the ruins of Mohenjodaro, is 60% that of the same ratio prevailing in the atmosphere. Calculate the age of the wood, given*

$T_{\frac{1}{2}}$ of $_6C^{14}$=5580 years.

**Answer.**

$$\text{We know that, } T_{\frac{1}{2}}=\frac{0{\cdot}693}{\lambda}$$

$$\text{or, } \lambda=\frac{0{\cdot}693}{T_{\frac{1}{2}}}=\frac{0{\cdot}693}{5580}\ /\text{ year}$$

$$\text{Also we have, } \lambda=\frac{2{\cdot}303}{t}\log\frac{No}{N} \quad \ldots\ \text{(A)}$$

Let the time for the $_6C^{14}$ : $_6C^{12}$ ratio to come down to 60% of that of the atmosphere be $t$ years. Under the conditions of the problem,

$$\frac{N_0}{N}=\frac{100}{60}.$$

Putting the values of $\lambda$ and $\frac{N_0}{N}$ in eqn (A),

we get,

$$\frac{0{\cdot}693}{5580}=\frac{2{\cdot}303}{t}\log\frac{100}{60}$$

$$\text{or, } t=\frac{5580\times2.303}{0{\cdot}693}\log\frac{10}{6}$$

$$=\frac{5580\times2{\cdot}303\times0{\cdot}2218}{0{\cdot}693}$$

$$=4112 \text{ years.}$$

## EXERCISES

1. Calculate the wt. in gms. of (*a*) 1 curie of RaB ($Pb^{214}$) from its $T_{\frac{1}{2}}=26{\cdot}8$ mins. [Ans. $4{\cdot}97\times10^{-10}$ gm.]

2. The half-life of $Sr^{90}$ is 19·9 years. Calculate the wt. of 1 mc of $Sr^{90}$. [Ans. $17.63\times10^{-16}$ gm.]

3. Calcultae (*a*) the mass defect and (*b*) the binding energy per nucleon of $Co^{59}$. Given, the mass of $_{27}Co^{59}$ from mass spectrographic measurement is 58·95182 amu. and $m_H=1{\cdot}008142$ amu. and $m_n=1.008982$ amu. 1 amu = 931 Mev. [Ans. (a) 0·555438 amu ; (b) 8.76459 Mev.]

4. Calculate the ratio of $U^{238}$ : $Ra^{226}$ atoms in natural uranium. Given : $T_{\frac{1}{2}}$ of $U^{238}=4{\cdot}49\times10^{9}$ years and $T_{\frac{1}{2}}$ of $Ra^{226}=1622$ years. [Ans. U : Ra $=3{\cdot}61\times10^{-7}$]

5. Find out the number of disintegrations occuring per minute in (*a*) 1 gm. of $Th^{232}$ ($T_{\frac{1}{2}}=1{\cdot}4\times10^{10}$ years) and (*b*) 1 μ gm. of $Ra^{226}$ ($T_{\frac{1}{2}}=1622$ years). [Ans. (*a*) $2{\cdot}45\times10^{6}$ dpm. and (*b*) $2{\cdot}17\times10^{6}$ dpm.]

6. Calculate the energy released in calories per mole of deuterium in the fusion reaction $_1H^2+{}_1H^2={}_2H^3+{}_0n^1$.

Atomic masses given : $_1H^2=2{\cdot}014735$ amu.
$_2He^3=3{\cdot}016977$ amu.
$_0n^1=1{\cdot}008982$ amu. [Ans. $7{\cdot}54\times10^{10}$ cals./mole]

## ACIDS AND BASES.

### Illustrations.

1. *Calculate the sulphide ion concentration in a 0.3M HCl solution saturated with $H_2S$. Given : $H_2S \rightleftharpoons H^+ + HS^-$*

$$K_1=\frac{[H^+][HS^-]}{[H_2S]}=9{\cdot}1\times10^{-8} \quad \cdot\cdot \quad \cdot\cdot \quad (1)$$

*and $HS^- \rightleftharpoons H^+ + S^{2-}$*

$$K_2=\frac{[H^+][S^{2-}]}{[HS^-]}=1{\cdot}2\times10^{-15} \quad \cdot\cdot \quad \cdot\cdot \quad (2)$$

*Concn. of $H_2S$ in the saturated soln. $=0{\cdot}1$ M.*

**Answer.**

$$K_1\times K_2=\frac{[H^+][HS^-]}{[H_2S]}\times\frac{[H^+][S^{2-}]}{[HS^-]}=9{\cdot}1\times10^{-8}\times1{\cdot}2\times10^{-15}$$

$$=1{\cdot}092\times10^{-22}\simeq1{\cdot}1\times10^{-22}$$

or, $$\frac{[H^+]^2\times[S^{2-}]}{[H_2S]}=1{\cdot}1\times10^{-22}$$

Here, $[H_2S]=0{\cdot}1$ $\therefore$ $$\frac{[H^+]^2\times[S^{2-}]}{0.1}=1{\cdot}1\times10^{-22}$$

or, $$[S^{2-}]=\frac{1{\cdot}1\times10^{-23}}{[H^+]^2} \quad \cdot\cdot \quad \cdot\cdot \quad (a)$$

In this problem, $[H^+]=0{\cdot}3$ (Since HCl is a strong acid $[HCl]=[H^+]$)

$$\therefore\ [S^{2-}]=\frac{1{\cdot}1\times10^{-23}}{(0{\cdot}3)^2}=\frac{1{\cdot}1\times10^{-23}}{9\times10^{-2}}=0{\cdot}122\times10^{-21}$$

Thus, the sulphide ion concentration in a 0·3M HCl solution saturated with $H_2S=0.122\times10^{-21}$ gm-ions/litre.

2. *Examine the effect of addition of 0·10 gm-mole of sodium acetate to 1 litre of 0·10 molar acetic acid on the degree of dissociation of acetic acid. Given, $K_a$ of acetic acid at $25°C=1{\cdot}80\times10^{-5}$.*

**Answer.**

$$\begin{array}{lcc} CH_3COOH \overset{\alpha}{\rightleftharpoons} CH_3COO^- & + & H^+ \\ C(1-\alpha)\qquad\qquad C\alpha & & C\alpha \end{array}$$

$$K_a=\frac{C\alpha^2}{1-\alpha}=1{\cdot}8\times10^{-5}$$

Here, concn. of acetic acid, $C=0{\cdot}10$ gm-mole/litre.

Since acetic acid is a weak acid, $\alpha$ is very small and $1-\alpha\approx1$.

Thus, $K_a=C\alpha^2=0{\cdot}10\times\alpha^2=1{\cdot}8\times10^{-5}$

$$\therefore\ \alpha^2=\frac{1{\cdot}8\times10^{-5}}{0{\cdot}10}\quad\text{or,}\quad \alpha=\sqrt{\frac{1{\cdot}8\times10^{-5}}{1\times10^{-1}}}\sqrt{=1{\cdot}8\times10^{-4}}$$

$$=0{\cdot}001344\approx0{\cdot}00134.$$

Since $[H^+]=C\alpha$, before the addition of $CH_3COONa$,
$[H^+]=0{\cdot}10\times0{\cdot}00134=0{\cdot}000134$ gm-ions/litre.

$\therefore\ [CH_3COOH]=C(1-\alpha)=(0{\cdot}1-0{\cdot}000134)\approx0{\cdot}10$ gm-mole/litre.

Let $\alpha'$ be the changed degree of dissociation of acetic acid after the addition of $CH_3COONa$. Since $CH_3COONa$ is a salt, it will dissociate more or less completely and hence, $[CH_3COONa]=[CH_3COO^-]$.

Now, after the addition of $CH_3COONa$,
$[H^+]=C\alpha'=0{\cdot}10\times\alpha'$.
Also, $[CH_3COO^-]=0{\cdot}10+0{\cdot}000134\simeq0{\cdot}10$ gm-ions/litre.
So, $[CH_3COOH]=0{\cdot}10(1-\alpha')\approx0{\cdot}1$ gm-moles/litre
(Since $\alpha'$ is very small).

$$\therefore\ K_a=\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}=\frac{(0{\cdot}10\alpha'\times0{\cdot}10)}{0{\cdot}10}=1{\cdot}80\times10^{-5}$$

$$\text{or,}\quad \alpha'=\frac{1{\cdot}8\times10^{-5}}{0{\cdot}10}=1{\cdot}8\times10^{-4}=0{\cdot}00018.$$

3. *Calculate the pH of a 0.02M solution of acetic acid, if its degree of dissociation is 12%.*

**Answer :**

$$\begin{array}{ccc} CH_3COOH & \overset{\alpha}{\rightleftharpoons} & CH_3COO^- + H^+ \\ C(1-\alpha) & & C\alpha \qquad C\alpha \end{array}$$

Here, $C = 0\cdot02M$. $\alpha = 12\% = 0\cdot12$.

$$[H^+] = C\alpha = 0\cdot02 \times 0\cdot12 = 0\cdot0024 = 2\cdot4 \times 10^{-3}$$

$$\therefore \ pH = -\log[H^+] = -\log(2\cdot4 \times 10^{-3})$$
$$= 3 - \log 2\cdot4 = 2\cdot62.$$

4. *Calculate (a) the hydrolysis constant, (b) the degree of hydrolysis and (c) the pH of a 0.2M solution of sodium acetate. Given, $K_a$ of acetic acid at 25°C $= 1\cdot82 \times 10^{-5}$.*

**Answer :**

$$K_a = 1\cdot82 \times 10^{-5} \quad \therefore \ pK_a = -\log(1\cdot82 \times 10^{-5}) = 4\cdot74.$$

(*a*) *Since $CH_3COONa$ is a salt of a weak acid and a strong base, its hydrolysis constant, $K_h = \frac{K_w}{K_a}$.*

$$\therefore \ K_h = \frac{1 \times 10^{-14}}{1\cdot82 \times 10^{-5}} = 0\cdot549 \times 10^{-9}$$

(*b*) Degree of hydrolysis, $\alpha = \sqrt{\frac{K_w}{K_a.C}} = \sqrt{\frac{1 \times 10^{-14}}{1\cdot82 \times 10^{-5} \times 2 \times 10^{-1}}}$

$$= 0\cdot524 \times 10^{-4}.$$

(*c*) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$

$$= 7 + \frac{4\cdot74}{2} + \frac{1}{2}\log(2 \times 10^{-1})$$
$$= 7 + 2\cdot37 - 0\cdot3495 = 9\cdot0205.$$

5. *24 ml. 0·2N NaOH is added to 25 ml. of 0·2N $CH_3COOH$. What is the pH of the resultant solution ? Given, $pK_a$ of acetic acid $= 4\cdot74$.*

**Answer :**

Since the strengths of NaOH and $CH_3COOH$ are equal and $= 0\cdot2N$, acetic acid remaining unreacted $= (25 - 24) = 1$ ml.

Total volume of the mixture $= (24 + 25) = 49$ ml.

$\therefore$ Strength of remaining acetic acid $= \frac{1 \times 0\cdot2}{49}$M, and strength of sodium acetate$=\dfrac{0{\cdot}1\times 48}{49}$M.

$$\therefore\ \ pH=pK+\log\ \frac{[\text{Salt}]}{[\text{Acid}]}=4.74+\log\ \frac{0{\cdot}1\times 48}{0{\cdot}2\times 1}$$

$$=4.74+\log\ \frac{4{\cdot}8}{0{\cdot}2}$$

$$=4{\cdot}74+\log 24=6{\cdot}1202.$$

## EXERCISES

1. Calculate the $p$H values of solutions containing : (*a*) $2\times 10^{-3}$ gm-ion of $H^+$ per litre, (*b*) $8.1\times 10^{-3}$ gm.-ion of $OH^-$ per litre.
[Ans. (*a*) 2·6990 ; (*b*) 11·9085.]

2. Two solutions have $p$H values of (*a*) 2·60 and (*b*) 12·50. What are the concentrations of $H^+$ and $OH^-$ ions in these solutions ?
[Ans. (*a*) $[H^+]=0.2512\times 10^{-2}$ and $[OH^-]=0.3981\times 10^{11}$ ;
(*b*) $[H^+]=0{\cdot}3162\times 10^{-12}$ and $[OH^-]=0{\cdot}3162\times 10^{-1}$]

3. Calculate the degree of dissociation of a 0·1N acetic acid and its dissociation constant, if its $p$H is 2·90. [Ans. $\alpha=1{\cdot}35$ percent ; $K_a=1{\cdot}8\times 10^{-5}$]

4. Calculate the $p$H of a 0·1(N) formic acid solution. Given $K_a=2\times 10^{-4}$.
[Ans. $p$H=2.85.]

5. What is the effect of addition of 0·1 gm-mole $NH_4Cl$ to 1 litre of a 0.1 molar ammonia solution, on the degree of dissociation $NH_4OH$ ? Given, $K_b=1{\cdot}8\times 10^{-5}$. [Ans. The degree of dissociation is changed from 1·35 percent to 0·018 percent.]

6. Calculate the $p$H of a mixture containing 0.1 M $NH_4OH$ and 0·1 M $NH_4Cl$.
[Ans. $p$H=10·25]

7. Calculate the degree of hydrolysis and $p$H of 0·2M solution of $NH_4Cl$. Given, $K_b=1{\cdot}8\times 10^{-5}$. [Ans. $\alpha=0{\cdot}00527$ percent and $p$H=4·997.]

8. Calculate the hydrolysis constant and the $p$H of a 0·1 M solution of ammonium acetate. Given, $pK_a$ of acetic acid=4·75 and $pK_b$ of $NH_4OH$=4·75.
[Ans. $K_h=3{\cdot}086\times 10^{-5}$; and $p$H=7.]

9. Calculate the concentration ratio of [H.COOH]/[H.COONa] required to prepare a solution of $p$H=2, given that, $K_{HCOOH}=2\times 10^{-4}$. [Ans. 50]

## OXIDATION REDUCTION.

### Illustration.

1. *Calculate, at 25°C, the equilibrium constant for the reaction* $Fe^{+3}+I^-=Fe^{+2}+\frac{1}{2}I_2$. *Given :*

$$E^\circ_{Fe^{+3}/Fe^{+2}}=0{\cdot}77 \text{ volts and } E^\circ_{I/I^-}=0{\cdot}535 \text{ volts at } 25^\circ C.$$

**Answer :**

We know that,

$$E_{Fe^{+3}/Fe^{+2}}=0{\cdot}77+0{\cdot}059\log\frac{[Fe^{+3}]}{[Fe^{+2}]}.$$

Also, $E_{I/I^-}=0{\cdot}535+0{\cdot}059\log\frac{[I]}{[I^-]}$.

Equilibrium constant of the reaction, $Fe^{+3}+I^- \rightleftharpoons Fe^{+2}+I$

$$K=\frac{[Fe^{+2}][I]}{[Fe^{+3}][I^-]}$$

At equilibrium $E_{Fe^{+3}/Fe^{+2}}=E_{I/I^-}$

$$\therefore\ 0{\cdot}77+0{\cdot}059\log\frac{[Fe^{+3}]}{[Fe^{+2}]}=0{\cdot}535+0{\cdot}059\log\frac{[I]}{[I^-]}$$

or, $(0{\cdot}77-0{\cdot}535)=0{\cdot}059\ \log\frac{[I][Fe^{+2}]}{[I^-][Fe^{+3}]}$

or, $0{\cdot}235=0{\cdot}059\log K$

or, $\log\ K=\frac{0{\cdot}235}{0{\cdot}059}=3{\cdot}98$

$\therefore\ K=$Antilog of $3{\cdot}98=0{\cdot}9550\times10^4$.

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2. *Calculate the oxidation potential of the $MnO_4^-/Mn^{+2}$ system, if $[MnO_4^-]=[Mn^{+2}]$ at hydrogen-ion concentrations of (a) 1 gm-ion per litre and (b) $10^{-4}$ gm-ion per litre. Given :*

$$E^\circ_{MnO_4^-/Mn^{+2}}=1{\cdot}52 \text{ volts at } 25^\circ C.$$

**Answer :**

The partial ionic eqn. for the reduction of the $MnO_4^-$ ion in acid medium is :

$$MnO_4^-+8H^++5e \longrightarrow Mn^{+2}+4H_2O.$$

The expression for the E.M.F. of this system is

$$E = E^\circ+\frac{0{\cdot}059}{5}\log\ \frac{[MnO_4^-][H^+]^8}{[Mn^{+2}]}$$

Here, $E^\circ=1{\cdot}52$ volts, and the number of electrons involved per mole of the oxidant, $MnO_4^-=5$. Also, $\frac{[MnO_4^-]}{[Mn^{+2}]}=1$.

$$\therefore\ E=1{\cdot}52+\frac{0{\cdot}059}{5}\log\ \frac{[MnO_4^-]}{[Mn^{+2}]}+\frac{0{\cdot}059}{5}\log[H^+]^8$$

$$=1{\cdot}52+\frac{0{\cdot}059}{5}\ \log[H^+]^8 \text{ (Since } \frac{0{\cdot}059}{5}\log 1=0).$$

(*a*) Here, $[H^+]=1 \quad \therefore \log [H^+]^8=\log 1=0$

$\therefore$ E=1·52 vols.

(*b*) Here, $[H^+]=10^{-4} \quad \therefore \log [H^+]^8=\log [10^{-4}]^8$

$$\begin{aligned}\therefore \quad E&=1{\cdot}52+\frac{0{\cdot}059}{5}\log [10^{-4}]^8\\ &=1{\cdot}52+\frac{0{\cdot}059}{5}\log 10^{-32}\\ &=1{\cdot}52+\frac{0{\cdot}059\times(-32)}{5}\\ &=1{\cdot}52-0{\cdot}3776\\ &=1{\cdot}1424 \text{ volts.}\end{aligned}$$

3. *A cell consists of a standard hydrogen electrode and the $Ni^{+2}/Ni$ system. With $[Ni^{+2}]=0{\cdot}01$ gm-ion per litre, its e.m.f. is 0.172 volt and the nickel electrode is the cathode. Find the standard oxidation potential of the $Ni^{+2}/Ni$ system.*

**Answer :**

The expression for the e.m.f. of the cell

$Ni/Ni \mid H^+(C=1) \mid H_2(1 \text{ atm.})$, is

$$E = E^\circ_{Ni^{+2}/Ni}+\frac{0.059}{2}\log [Ni^{+2}]$$

Here, E=0·172 volts and $[Ni^{+2}]=0{\cdot}01=10^{-2}$ gm-ion/litre.

$$\therefore \; 0{\cdot}172 = E^\circ_{Ni^{+2}/Ni}+\frac{0{\cdot}059}{2}\log (1\times 10^{-2})$$

$$= E^\circ+\frac{0{\cdot}059}{2}\log 1+\frac{0{\cdot}0592}{2}\log 10^{-2}$$

$$= E^\circ+0+0{\cdot}059$$

$$\therefore \quad E^\circ = 0{\cdot}172+0{\cdot}059$$

$$= 0.231 \text{ volts.}$$

Since the $Ni^{+2}/Ni$ electrode is the cathode, the standard oxidation potential of the $Ni^{+2}/Ni$ system is $-0{\cdot}231$ volts.

4. *A sample of $KMnO_4$ was heated with conc. HCl and the issuing gas was absorbed into a potassium iodide solution. After completion of reaction, the liberated iodine was titrated with a solution of $Na_2S_2O_3, 5H_2O$, containing 62 gms. per litre. Exactly 60 ml. of the thiosulphate solution were required to decolorise the iodine in solution. What weight of $KMnO_4$ was used ?*

*[K=39, Na=23, Mn=55, H=1, O=16, Cl=35.5, I=127 and S=32].*

**Answer :**

Mol. wt. of $Na_2S_2O_3$=248.
Mol. wt. of $KMnO_4$=158.

The reaction between thiosulphate and iodine is :

$$I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$$

The oxidation of the thiosulphate ion to the tetrathionate ion, is represented in ion-electron method as : $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-}+2e$.

∴ One electron is involved in the oxidation of one thiosulphate ion.

Thus, eq. wt. of $Na_2S_2O_3$, $5H_2O=\frac{\text{Mol. wt.}}{1}=248$.

∴ Strength of the thiosulphate solution used $=\frac{62}{248}$ (N)=0·25(N).

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Also the equivalent wt. of $KMnO_4$ in its reaction with $Cl^-$ (HCl) : $2KMnO_4+16HCl=2KCl+2MnCl_2+8H_2O+5Cl_2\uparrow$, is obtained from the partial ionic eqn.

$$MnO_4^-+8H^++5e \longrightarrow Mn^{+2}+4H_2O,$$

as, $\frac{\text{Mol. wt.}}{5}=\frac{158}{5}=31{\cdot}6$.

Now, 60 ml. of 0·25 (N) thiosulphate soln.

≡(60×0·25) ml. (N) thiosulphate soln.
≡15 ml. (N) thiosulphate soln.
≡15 ml. (N) iodine soln.
≡15 ml. (N) $KMnO_4$ soln.

1000 ml. (N) $KMnO_4$ soln. ≡ 31·6 gms. $KMnO_4$

∴ 15 ml. (N) ,, ,, $\equiv\frac{31{\cdot}6\times15}{1000}$ gm. $KMnO_4$.

=0·4740 gm. ,,

Thus, the weight of $KMnO_4$ used in this case is 0·4740 gm.

5. *To 0·5 gm. sample of pyrolusite is added a certain weight of hydrated oxalic acid. After the reaction in acid solution is completed, the excess oxalic acid required 30·0 ml of 0·1(N)* $KMnO_4$ *for complete oxidation. If the pyrolusite contained 86·93 percent* $MnO_2$, *calculate the weight of the oxalic acid added.*

**Answer :**

Hydrated oxalic acid has the formula $(COOH)_2.\ 2H_2O$ and hence, its molecular wt. is 126.

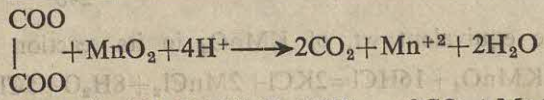
100 gms. pyrolusite contain 86·93 gms. $MnO_2$

∴ 0·5 gm. ,, ,, $0{\cdot}8693 \times 0{\cdot}5 = 0{\cdot}4346$ gm. $MnO_2$.

The partial ionic eqns. for the oxidation of the oxalate ion (each mole of hydrated oxalic acid yielding one oxalate ion) and the reduction of $MnO_2$ are :

$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array} \longrightarrow 2CO_2 + 2e \quad \ldots \quad \ldots \quad (A)$$

$$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{+2} + 2H_2O. \quad \ldots \quad \ldots \quad (B)$$



$$\begin{array}{l} COO \\ | \\ COO \end{array} + MnO_2 + 4H^+ \longrightarrow 2CO_2 + Mn^{+2} + 2H_2O$$

$$\text{or,}\quad \underset{126}{(COOH)_2.\ 2H_2O} + \underset{86{\cdot}93}{MnO_2} + 2H^+ = 2CO_2 + Mn^{+2} + 4H_2O$$

Hence, 86·93 gms. $MnO_2 \equiv 126$ gms. of hydrated oxalic acid

∴ 0·4346 gm. ,, $= \frac{126}{86{\cdot}93} \times 0{\cdot}4346 = 0{\cdot}6299$ gm. ,,

Again, 30·0 ml. 0.1 (N) $KMnO_4 \equiv (30 \times 0{\cdot}1)$ ml. (N) $KMnO_4$

$\equiv 3$ ml. (N) $KMnO_4$

$= 3$ ml. (N) oxalic acid

From eqn. (A), the eq. wt. of oxalic acid$= \frac{126}{2} = 63.$

∴ 1000 ml. (N) oxalic acid soln. contain 63 gms. of oxalic acid.

∴ 3 ml. (N) .. .. $\frac{63}{1000} \times 3$

$= 0{\cdot}189$ gm. oxalic acid.

∴ Total weight of hydrated oxalic acid used here is $0{\cdot}6299 + 0{\cdot}189 = 0{\cdot}8189$ gm.

## EXERCISES

1. Calculate the equilibrium constant of the redox reaction :

$$2Fe^{+3}+Sn^{+2} = 2Fe^{+2}+Sn^{+4}.$$

Given, $E^\circ_{Fe^{+3}/Fe^{+2}} = 0{\cdot}77$ volts at $25^\circ C = E^\circ_1$

and $E^\circ_{Sn^{+4}/Sn^{+2}} = 0{\cdot}15$ volts at $25^\circ C = E^\circ_2$

[Ans. $1{\cdot}04 \times 10^{21}$]

2. Calculate the oxidation potential of the system $Sn^{+4}/Sn^{+2}$, if the $[Sn^{+4}] = 0{\cdot}1$ gm.-ion/litre and the $[Sn^{+2}] = 0{\cdot}0001$ gm-ion/litre. [Ans. 0·237v]

3. Calculate the percentage of iron in a sample of iron powder, if the titration of the $FeSO_4$ solution, obtained by dissolving 0·1400 gm. of the powder in $H_2SO_4$ (in absence of air), required 24·85 ml. of 0·100(N) $KMnO_4$ solution. [Ans. 99·15%]

4. 0·200 gm. of a pyrolusite ore is heated to 60 – 70°C with a mixture of oxalic acid soln. and $H_2SO_4$. The volume of oxalic acid used was 25·0 ml. and the titration of excess oxalic acid required 2 ml. of 0·2(N) $KMnO_4$. If 25 ml. of the oxalic acid used are equivalent to 4·5 ml. of the $KMnO_4$ employed, find the percentage of Mn in the ore. [Ans. 6·87% Mn]

5. 0·2 gm. of a pyrolusite ore was treated with concentrated HCl and the chlorine liberated in the reaction was passed into a KI solution. Titration of the liberated iodine required 42·50 ml. of 0·052N thiosulphate solution. Calculate the % of $MnO_2$ in the ore. [Ans. 45·67%]

|  |  | 1s | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 4f | 5s | 5p | 5d | 5f | 6s | 6p | 6d | 7s |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | 1 H | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 2 He | 2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 1s Full |
|  | 3 Li | 2 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 4 Be | 2 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 2s Full |
|  | 5 B | 2 | 2 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 6 C | 2 | 2 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 7 N | 2 | 2 | 3 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 8 O | 2 | 2 | 4 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 9 F | 2 | 2 | 5 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 10 Ne | 2 | 2 | 6 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 2p Full |
|  | 11 Na | 2 | 8 |  | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 12 Mg | 2 | 8 |  | 2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 3s Full |
|  | 13 Al | 2 | 8 |  | 2 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 14 Si | 2 | 8 |  | 2 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 15 P | 2 | 8 |  | 2 | 3 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 16 S | 2 | 8 |  | 2 | 4 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 17 Cl | 2 | 8 |  | 2 | 5 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 18 Ar | 2 | 8 |  | 2 | 6 |  |  |  |  |  |  |  |  |  |  |  |  |  | 3p Full |
|  | 19 K | 2 | 8 |  | 8 |  |  | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 20 Ca | 2 | 8 |  | 8 |  |  | 2 |  |  |  |  |  |  |  |  |  |  |  | 4s Full |
| Transition elements | 21 Sc | 2 | 8 |  | 8 |  | 1 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 22 Ti | 2 | 8 |  | 8 |  | 2 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 23 V | 2 | 8 |  | 8 |  | 3 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 24 Cr | 2 | 8 |  | 8 |  | 5 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 25 Mn | 2 | 8 |  | 8 |  | 5 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 26 Fe | 2 | 8 |  | 8 |  | 6 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 27 Co | 2 | 8 |  | 8 |  | 7 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 28 Ni | 2 | 8 |  | 8 |  | 8 | 2 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 29 Cu | 2 | 8 |  | 8 |  | 10 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 30 Zn | 2 | 8 |  | 8 |  | 10 | 2 |  |  |  |  |  |  |  |  |  |  |  | 3d Full |
|  | 31 Ga | 2 | 8 |  | 18 |  |  | 2 | 1 |  |  |  |  |  |  |  |  |  |  |  |
|  | 32 Ge | 2 | 8 |  | 18 |  |  | 2 | 2 |  |  |  |  |  |  |  |  |  |  |  |
|  | 33 As | 2 | 8 |  | 18 |  |  | 2 | 3 |  |  |  |  |  |  |  |  |  |  |  |
|  | 34 Se | 2 | 8 |  | 18 |  |  | 2 | 4 |  |  |  |  |  |  |  |  |  |  |  |
|  | 35 Br | 2 | 8 |  | 18 |  |  | 5 | 5 |  |  |  |  |  |  |  |  |  |  |  |
|  | 36 Kr | 2 | 8 |  | 18 |  |  | 2 | 6 |  |  |  |  |  |  |  |  |  |  | 4p Full |
|  | 37 Rb | 2 | 8 |  | 18 |  |  | 8 |  |  |  | 1 |  |  |  |  |  |  |  |  |
|  | 38 Sr | 2 | 8 |  | 18 |  |  | 8 |  |  |  | 2 |  |  |  |  |  |  |  | 5s Full |
| Transition elements | 39 Y | 2 | 8 |  | 18 |  |  | 8 |  | 1 |  | 2 |  |  |  |  |  |  |  |  |
|  | 40 Zr | 2 | 8 |  | 18 |  |  | 8 |  | 2 |  | 2 |  |  |  |  |  |  |  |  |
|  | 41 Nb | 2 | 8 |  | 18 |  |  | 8 |  | 4 |  | 1 |  |  |  |  |  |  |  |  |
|  | 42 Mo | 2 | 8 |  | 18 |  |  | 8 |  | 5 |  | 1 |  |  |  |  |  |  |  |  |
|  | 43 Tc | 2 | 8 |  | 18 |  |  | 8 |  | 6 |  | 1 |  |  |  |  |  |  |  |  |
|  | 44 Ru | 2 | 8 |  | 18 |  |  | 8 |  | 7 |  | 1 |  |  |  |  |  |  |  |  |
|  | 45 Rh | 2 | 8 |  | 18 |  |  | 8 |  | 8 |  | 1 |  |  |  |  |  |  |  |  |
|  | 46 Pd | 2 | 8 |  | 18 |  |  | 8 |  | 10 |  |  |  |  |  |  |  |  |  |  |
|  | 47 Ag | 2 | 8 |  | 18 |  |  | 8 |  | 10 |  | 1 |  |  |  |  |  |  |  |  |
|  | 48 Cd | 2 | 8 |  | 18 |  |  | 8 |  | 10 |  | 1 |  |  |  |  |  |  |  | 4d Full |
|  | 49 In | 2 | 8 |  | 18 |  |  | 18 |  |  |  | 2 | 1 |  |  |  |  |  |  |  |
|  | 50 Sn | 2 | 8 |  | 18 |  |  | 18 |  |  |  | 2 | 2 |  |  |  |  |  |  |  |

IN ATOMS OF THE ELEMENTS IN THEIR NORMAL STATES

Transition elements

Rare earths or lanthanons

Actinons

| | 1s | 2s 2p | 3s 3p 3d | 4s 4p 4d 4f | | 5s 5p 5d 5f | | | | 6s 6p 6d | | | 7s | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 51 Sb | 2 | 8 | 18 | 18 | | 2 | 3 | | | | | | | |
| 52 Te | 2 | 8 | 18 | 18 | | 2 | 4 | | | | | | | |
| 53 I | 2 | 8 | 18 | 18 | | 2 | 5 | | | | | | | |
| 54 Xe | 2 | 8 | 18 | 18 | | 2 | 6 | | | | | | | *5p* Full |
| 55 Cs | 2 | 8 | 18 | 18 | | 8 | | | | 1 | | | | |
| 56 Ba | 2 | 8 | 18 | 18 | | 8 | | | | 2 | | | | *6s* Full |
| 57 La | 2 | 8 | 18 | 18 | | 8 | | 1 | | 2 | | | | |
| 58 Ce | 2 | 8 | 18 | 18 | 2 | 8 | | | | 2 | | | | |
| 59 Pr | 2 | 8 | 18 | 18 | 3 | 8 | | | | 2 | | | | |
| 60 Nd | 2 | 8 | 18 | 18 | 4 | 8 | | | | 2 | | | | |
| 61 Pm | 2 | 8 | 18 | 18 | 5 | 8 | | | | 2 | | | | |
| 62 Sm | 2 | 8 | 18 | 18 | 6 | 8 | | | | 2 | | | | |
| 63 Eu | 2 | 8 | 18 | 18 | 7 | 8 | | | | 2 | | | | |
| 64 Gd | 2 | 8 | 18 | 18 | 7 | 8 | | 1 | | 2 | | | | |
| 65 Tb | 2 | 8 | 18 | 18 | 9 | 8 | | | | 2 | | | | |
| 66 Dy | 2 | 8 | 18 | 18 | 10 | 8 | | | | 2 | | | | |
| 67 Ho | 2 | 8 | 18 | 18 | 11 | 8 | | | | 2 | | | | |
| 68 Er | 2 | 8 | 18 | 18 | 12 | 8 | | | | 2 | | | | |
| 69 Tm | 2 | 8 | 18 | 18 | 13 | 8 | | | | 2 | | | | |
| 70 Yb | 2 | 8 | 18 | 18 | 14 | 8 | | | | 2 | | | | |
| 71 Lu | 2 | 8 | 18 | 18 | 14 | 8 | | 1 | | 2 | | | | *4f* Full |
| 72 Hf | 2 | 8 | 18 | 32 | | 8 | | 2 | | 2 | | | | |
| 73 Ta | 2 | 8 | 18 | 32 | | 8 | | 3 | | 2 | | | | |
| 74 W | 2 | 8 | 18 | 32 | | 8 | | 4 | | 2 | | | | |
| 75 Re | 2 | 3 | 18 | 32 | | 8 | | 5 | | 2 | | | | |
| 76 Os | 2 | 8 | 18 | 32 | | 8 | | 6 | | 2 | | | | |
| 77 Ir | 2 | 8 | 18 | 32 | | 8 | | 7 | | 2 | | | | |
| 78 Pt | 2 | 8 | 18 | 32 | | 8 | | 9 | | 1 | | | | |
| 79 Au | 2 | 8 | 18 | 32 | | 8 | | 10 | | 1 | | | | |
| 80 Hg | 2 | 8 | 18 | 32 | | 8 | | 10 | | 2 | | | | *5d* Full |
| 81 Tl | 2 | 8 | 18 | 32 | | 18 | | | | 2 | 1 | | | |
| 82 Pb | 2 | 8 | 18 | 32 | | 18 | | | | 2 | 2 | | | |
| 83 Bi | 2 | 8 | 18 | 32 | | 18 | | | | 2 | 3 | | | |
| 84 Po | 2 | 8 | 18 | 32 | | 18 | | | | 2 | 4 | | | |
| 85 At | 2 | 8 | 18 | 32 | | 18 | | | | 2 | 5 | | | |
| 86 Rn | 2 | 8 | 18 | 32 | | 18 | | | | 2 | 6 | | | *6p* Full |
| 87 Fr | 2 | 8 | 18 | 32 | | 18 | | | | 8 | | | 1 | |
| 8 Ra | 2 | 8 | 18 | 32 | | 18 | | | | 8 | | | 2 | *7s* Full |
| 89 Ac | 2 | 8 | 18 | 32 | | 18 | | | | 8 | | 1 | 2 | |
| 90 Th | 2 | 8 | 18 | 32 | | 18 | | | | 8 | | 2 | 2 | |
| 91 Pa | 2 | 8 | 18 | 32 | | 18 | | | 2 | 8 | | 1 | 2 | |
| 92 U | 2 | 8 | 18 | 32 | | 18 | | | 3 | 8 | | 1 | 2 | |
| 93 Np | 2 | 8 | 18 | 32 | | 18 | | | 5 | 8 | | | 2 | |
| 94 Pu | 2 | 8 | 18 | 32 | | 18 | | | 6 | 8 | | | 2 | |
| 95 Am | 2 | 8 | 18 | 32 | | 18 | | | 7 | 8 | | | 2 | |
| 96 Cm | 2 | 8 | 18 | 32 | | 18 | | | 7 | 8 | | 1 | 2 | |
| 97 Bk | 2 | 8 | 18 | 32 | | 18 | | | 9 | 8 | | | 2 | |
| 98 Cf | 2 | 8 | 18 | 32 | | 18 | | | 10 | 8 | | | 2 | |
| 99 Es | 2 | 8 | 18 | 32 | | 18 | | | 11 | 8 | | | 2 | |
| 100 Fm | 2 | 8 | 18 | 32 | | 18 | | | 12 | 8 | | | 2 | |
| 101 Md | 2 | 8 | 18 | 32 | | 18 | | | 13 | 8 | | | 2 | |
| 102 No | 2 | 8 | 18 | 32 | | 18 | | | 14 | 8 | | | 2 | |

## TABLE OF ATOMIC WEIGHTS (based on carbon 12=12·0000).

| Element | Sym-bol | Atomic Number | Atomic Weight | Element | Sym-bol | Atomic Number | Atomic Weight |
|---|---|---|---|---|---|---|---|
| Actinium | Ac | 89 | 227 | Mercury | Hg | 80 | 200.59 |
| Aluminium | Al | 13 | 26.98 | Molybdenum | Mo | 42 | 95.94 |
| Americium | Am | 95 | (243) | Neodymium | Nd | 60 | 144.24 |
| Antimony | Sb | 51 | 121.77 | Neon | Ne | 10 | 20.183 |
| Argon | Ar | 18 | 39.946 | Neptunium | Np | 93 | (237)* |
| Arsenic | As | 33 | 74.92 | Nickel | Ni | 28 | 58.71 |
| Astatine | At | 85 | (210)* | Niobium | Nb | 41 | 92.91 |
| Barium | Ba | 56 | 137.34 | Nitrogen | N | 7 | 14.007 |
| Berkelium | Bk | 97 | (249)* | Nobelium | No | 102 | (253)* |
| Beryllium | Be | 4 | 9.012 | Osmium | Os | 76 | 190.2 |
| Bismuth | Bi | 83 | 208.98 | Oxygen | O | 8 | 15.99943 |
| Boron | B | 5 | 10.81 | Palladium | Pd | 46 | 106.4 |
| Bromine | Br | 35 | 79.909 | Phosphorus | P | 15 | 30.974 |
| Cadmium | Cd | 48 | 112.40 | Platinum | Pt | 78 | 195.09 |
| Calcium | Ca | 20 | 40.08 | Plutonium | Pu | 94 | (242)* |
| Californium | Cf | 98 | (251)* | Polonium | Po | 84 | 210 |
| Carbon | C | 6 | 12.01115 | Potassium | K | 19 | 39.102 |
| Cerium | Ce | 58 | 140.12 | Praseodymium | Pr | 59 | 140.907 |
| Caesium | Cs | 55 | 132.91 | Promethium | Pm | 61 | (147)* |
| Chlorine | Cl | 17 | 35.453 | Protactinium | Pa | 91 | (231)* |
| Chromium | Cr | 24 | 52.00 | Radium | Ra | 88 | 226.05 |
| Cobalt | Co | 27 | 58.933 | Radon | Rn | 86 | 222 |
| Copper | Cu | 29 | 63.54 | Rhenium | Re | 75 | 186.23 |
| Curium | Cm | 96 | (247)* | Rhodium | Rh | 45 | 102.92 |
| Dysprosium | Dy | 66 | 162.50 | Rubidium | Rb | 37 | 85.47 |
| Einsteinium | Es | 99 | (254) | Ruthenium | Ru | 44 | 101.07 |
| Eribium | Er | 68 | 167.26 | Samarium | Sm | 62 | 150.35 |
| Europium | Eu | 63 | 152.0 | Scandium | Sc | 21 | 44.956 |
| Fermium | Fm | 100 | (253)* | Selenium | Se | 34 | 78.96 |
| Fluorine | F | 9 | 19.02 | Silicon | Si | 14 | 28.086 |
| Francium | Fr | 87 | (223)* | Silver | Ag | 47 | 107.87 |
| Gadolinium | Gd | 64 | 157.25 | Sodium | Na | 11 | 22.9898 |
| Gallium | Ga | 31 | 69.72 | Strontium | Sr | 38 | 87.62 |
| Germanium | Ge | 32 | 72.59 | Sulphur | S | 16 | 32.064 |
| Gold | Au | 79 | 196.97 | Tantalum | Ta | 73 | 180.948 |
| Hafnium | Hf | 72 | 178.49 | Technetium | Tc | 43 | (99)* |
| Helium | He | 2 | 4.003 | Tellurium | Te | 52 | 127.60 |
| Holmium | Ho | 67 | 164.93 | Tebium | Tb | 65 | 158.94 |
| Hydrogen | H | 1 | 1.007967 | Thallium | Tl | 81 | 204.37 |
| Indium | In | 49 | 114.82 | Thorium | Th | 90 | 232.038 |
| Iodine | I | 53 | 126.90 | Thulium | Tm | 69 | 168.934 |
| Iridium | Ir | 77 | 192.20 | Tin | Sn | 50 | 118.69 |
| Iron | Fe | 26 | 55.85 | Titanium | Ti | 22 | 49.90 |
| Krypton | Kr | 36 | 83.80 | Tungsten | W | 74 | 183.85 |
| Lanthanum | La | 57 | 138.91 | Uranium | U | 92 | 238.08 |
| Lawrencium | Lw | 103 | (257)* | Vanadium | V | 23 | 50.942 |
| Lead | Pb | 82 | 207.19 | Xenon | Xe | 54 | 131.30 |
| Lithium | Li | 3 | 6.939 | Ytterbium | Yb | 70 | 173.04 |
| Lutecium | Lu | 71 | 174.97 | Yttrium | Y | 39 | 88.905 |
| Magnesium | Mg | 12 | 24.312 | Zinc | Zn | 30 | 65.37 |
| Manganese | Mn | 25 | 54.94 | Zirconium | Zr | 40 | 91.22 |
| Mendelevium | Md | 101 | (256)* |  |  |  |  |

*Figures in the parantheses are the mass numbers of the most stable isotope known.